BIOGAS PRODUCTION FROM SOME WASTE MATERIALS

THESIS
Submitted in partial fulfilment of the
requirements for the degree of
DOCTOR OF PHILOSOPHY

By
TANUSRI MANDAL

Under the Supervision of
Dr. V.S. Rao

BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE
PILANI (RAJASTHAN) INDIA

1996

BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE

PILANI (RAJASTHAN)

CERTIFICATE

This is to certify that the thesis entitled " BIOGAS PRODUCTION FROM SOME WASTE MATERIALS" submitted by TANUSRI MANDAL, ID No. 88PHXF408 for award of Ph.D. degree of the Institute, embodies original work done by her under my supervision.

Date: 29.07.96

Dr. V.S.Rao
Professor
Department of Chemistry

ACKNOWLEDGEMENTS

The author expresses her deep sense of gratitude to Dr. V.S. Rao for his untiring guidance and constant encouragement during the whole work of the Ph.D. Thesis.

The author sincerely thanks Dr. S. Venkateswaran, Director, Birla Institute of Technology & Science, Pilani for permitting her to work in this area and providing all the necessary facilities for this investigation.

The author expresses her heart-felt gratefulness to Dr. L.K. Maheshwari, Dean, Research and Consultancy Division, for his continuous evaluation of the progress of her Ph.D. work. She is also deeply thankful to Prof. K.E. Raman, Dean, Engineering Services Division for providing a number of instruments for the laboratory work and to Dr. (Mrs.) A. Gupta, Dean, Educational Hardware Division, for her encouragement throughout the thesis work. The author is also thankful to Dr. Y.Sivaji and Dr. K.R. Chandoke for their constructive suggestions for this thesis work.

The author's thanks are also due to Dr. (Mrs.) M. Banerji for having gone through the text of the thesis and giving useful suggestions in completing this work and to Dr. N.K. Mandal without whose help this thesis work would have not been completed.

Thanks are also due to Mr. S.D. Dewan for making neat tracings and to Mr. D.P.Soni for his excellent word-processing of this thesis.

The author also takes this opportunity to express sincere thanks to her parents, brothers, sisters and other relatives for their continuous encouragement during the whole period of work.

Lastly, the author puts on record the help and co-operation provided by her two beloved daughters Ranjusree and Srayasree at each step of this work.

Engineering Technology Group

Date:

T. Mandal
(Tanusri Mandal)

CONTENTS

Page No.

List of the figures:

CHAPTER - 1

REVIEW ON BIOGAS PRODUCTION FROM SOME WASTE MATERIALS

CHAPTER-1

Review on Biogas Production from some Waste Materials

1.1 INTRODUCTION :

With the ever increasing per capita consumption of energy and exponentially rising population, Scientists and Technologists already see world-wide shortage of energy. Due to this many alternative fuel sources are receiving attention. Among these, conversion of waste materials into biogas via anaerobic digestion has attracted universal attention in recent past [1-4].

Biogas represents a potential solution not only for the energy problem, but simultaneously to the problem of waste disposal. It can help in controlling environmental pollution which is a great threat to human life.

In an agricultural country like India, biogas can possibly be utilized to meet at least the energy requirements of rural areas. The biogas production is neither capital intensive nor is it a highly complex technological process. As such it holds a great promise for developing nations like India.

Rural areas usually have large supplies of crop residues and animal wastes theoretically suitable for their conversion into an usable source of energy. The process that appears to hold the greatest immediate potential for utilization of these materials as sources of fuel is anaerobic fermentation(biogas).

Waste materials are cheap sources of energy. Such waste materials are produced in large amounts by dairy farms, agricultural farms, industries, etc.

A biogas unit is an asset to a farming family. It is a new source of fuel for mechanisation of agriculture and village industries. It can be used for running diesel and petrol engines. Even electricity can be generated from it. It produces good manure and improves sanitation.

The best use of biogas is for cooking. In order to get the maximum heat value of this gas, it should be used in properly designed stoves.

Presently, agricultural residues and dung cakes are used as cooking fuels in rural areas. It is a wasteful practice as hardly 9-12% of their fuel value is harnessed. Moreover, smoky kitchens are harmful for the health of women and children. Also, a collection and storage of these materials is problematic especially during the rainy season.

A biogas unit helps in eliminating the age-old practice of burning cattle dung, agricultural wastes, etc. for fuel purposes. It is a clean and efficient fuel for the purpose of cooking. It saves the consumption of kerosine, charcoal and wood. It would eliminate the practice of indiscriminate felling of trees and the consequent soil errosion.

There is a big demand for biogas lamps in unelectrified rural areas. Children can read and write with the help of a biogas illumination, during erratic supply of electricity or shortage of kerosine. However, the light produced is not as good as that from an electric bulb.

Biogas is an excellent and economic fuel for both petrol and diesel engines. Petrol engines can be run 100% on biogas except that a little petrol is consumed in starting it up. Diesel engines are modified to dual-fuel engines which use both biogas and diesel oil. Dual-fuel engines are also known as "Gobar gas engines". The capacities of such engines range from 3 to 96 H.P. A dual-fuel engine can be used for running an irrigation pump, flour mill, chaff-cutter, thresher, etc. Dual-fuel generators help in the production of electricity from biogas. Generators of capacities ranging from 3.5 to 7.5 KVA are available in the market.

Biogas units are effective means for the sanitary disposal of human excreta. In areas with dry latrines, the practice of carrying head loads of night-soil can be eliminated by attaching latrines with a biogas unit. By putting all human and animal excreta into a biogas unit the problem of waste disposal is solved at the family level itself.

During decomposition of night-soil in a biogas unit, most of the disease-causing organisms are killed. This can serve as an effective control of parasitic diseases, hook warm, roundworm, etc. The digested slurry remains free from foul smell and most of the pathogens. Mosquitoes and flies do not breed in digested slurry. Thus biogas units improve sanitation.

Biogas being a clean fuel, does not cause air pollution. It is considered a better fuel than natural gas and liquified petroleum gas because it does not contain sulphur. The incidence of eye diseases among women and children is also reduced as the use of biogas does not cause any smoke in the kitchen. The danger of explosion of biogas is less as it contains carbon dioxide which acts as a fire extinguisher.

Farmers consider the importance of biogas units in terms of the availability of larger quantities of better quality of manure. Generally speaking, one-third of half of all cattle dung is burned as fuel and is thus lost to soil. On the other hand, a biogas plant in many situations doubles the avail ability of organic manure.

The manure produced through a biogas unit has a comparative advantage over ordinary manure in terms of both quantity and quality. About 70-75% of the original weight of cattle dung is conserved in a biogas unit, while in open compostpits 50% or more is lost. Similarly, almost all the nitrogen content in cattle dung is conserved in a biogas unit, while a substantial part of this is lost during composting biogas manure, known as "digested slurry" which contains a higher percentage of other plant nutrients also. It is a good source of micro-nutrients like zinc, iron, manganese and copper which are slowly decreasing in many different kinds of soils. Also, the complete digestion of cattle dung in biogas units kills seeds of weeds. Organisms causing plant diseases are also killed.

It has been observed that the use of digested slurry as manure improves soil fertility and increases crop yield by 10- 20%.

Digested slurry has been found useful for raising fish. Common carp fry and fingerlings fed on a mixture of rice bran and digested slurry (1:3) and mustard oil cake and rice bran (1:1) showed faster growth with the bran-slurry mixture. The recommended ideal feed for singi fish is equal quantifies of mustard oil cake, bran and digested slurry.

There are various types of waste materials, but all waste materials are not bio-degradable. Only bio-degradable waste materials can produce biogas[14]. Due to the presence of lignin, some waste materials are not bio-degradable. So it is required to pre-treat these waste materials to remove lignin before using them in the biogas digester to produce biogas.

In this Chapter, a rigorous effort has been made to review the work done on various aspects of biogas generating systems, their constructions, performances and the applications for utilizing different waste materials.

1.2 Biogas: Energy recovery from waste materials

Biogas is a term used to describe a mixture of gases which is produced when organic matters, such as animal wastes, agricultural wastes, etc., are broken down or digested by bacteria in the absence of oxygen. This process is known as anaerobic digestion. Biogas normally contains by volume 50-75 per cent of methane (CH_4) and 25-50 per cent of carbon-di-oxide (CO_2) with small amounts of other gases such as hydrogen sulphide, carbon monoxide, etc.[15].

Biogas plants in city sewage treatment plants are called "Sludge-digesters". Other names for biogas are 'Bihugas' in Federal Republic of Germany, "Gobar-gas in India, "Marsh-gas in China[16].

1.2.1 Basic mechanisms of biogas formation :

Biogas producation is a microbial process . The Fig. 1.1 shows the process which involves the combined action of four groups of bacteria, in four stages , in a biogas plant [20].

First stage : In this stage degradation of high molecular weight substances like cellulose, starch, proteins, fats, etc. present in the organic materials, takes place and small molecular weight compounds like fatty acids, amino acids, Co_2 and H_2 are produced by the hydrolytic bacteria.

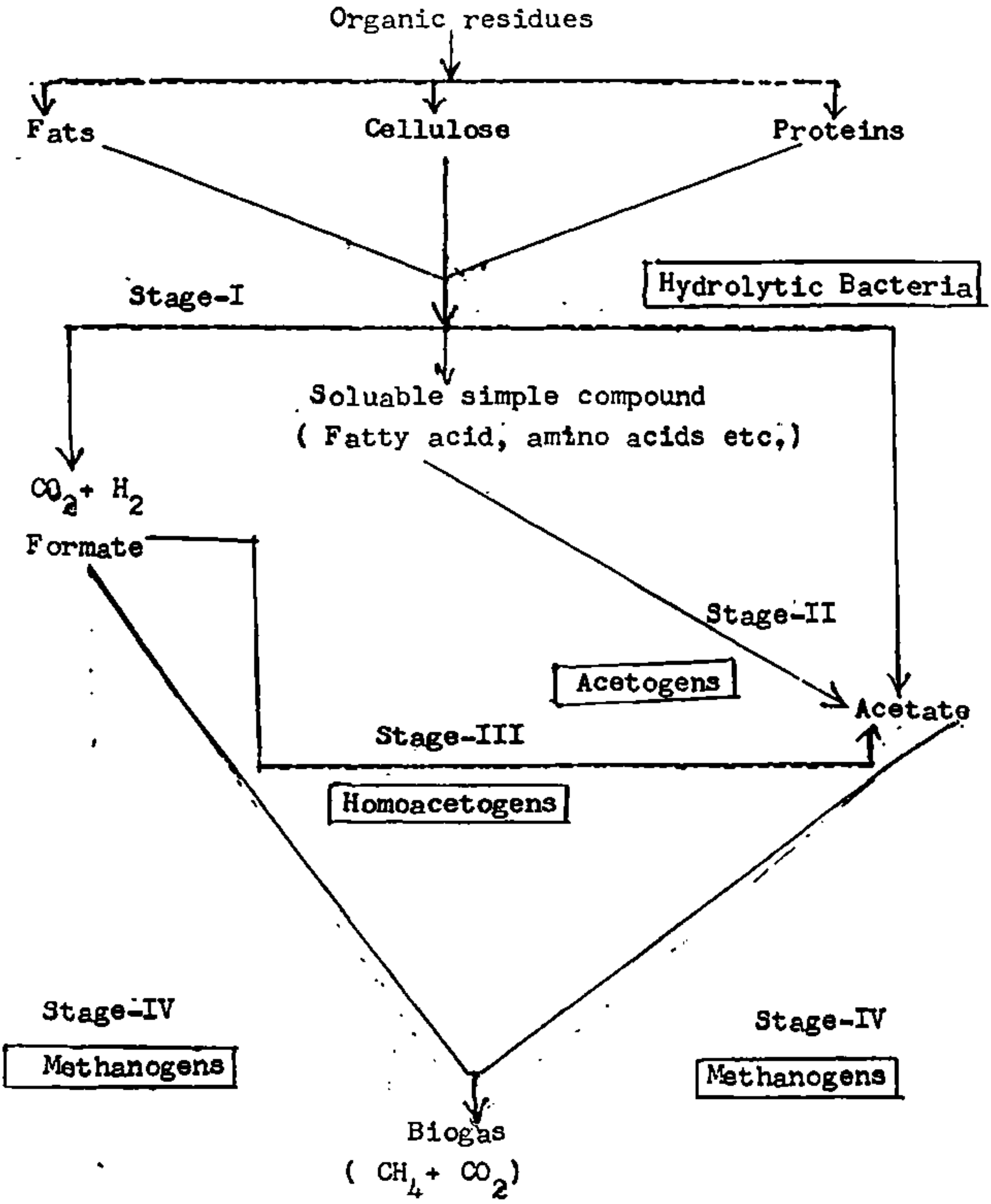


Fig 1.1 : Four stages of biogas production from organic residues.

Second Stage: In this stage, the end products of the first stage are converted into acetate by acetogens.

Third Stage : In this stage, microorganisms known as homoacetogens convert hydrogen , carbon- dioxide and simple carbon compounds produced in first and second stages into acetate. This stage is involved in producing more acetate.

Fourth Stage : In this stage , the conversion of acetate and some other compounds like formate, carbon-dioxide and hydrogen into methane takes place. This is brought about by a unique group of bacteria known as methanogens.

1.2.2 Feedstock:

For generation of biogas animal and human wastes such as cow dung, buffalo dung, urine, poultry dropping free from litter, horse dung free from bedding material, other live stock excreta, night-soil, etc., are used as feedstock.

It is desirable to use a mixture of excreta in order to get more gas because, as compared to cattle dung (100%), the gas production is 60% from poultry droppings, 70% from goat excreta, 150% from horse dung and 250% from pig dung [10]. In order to utilize other materials like water hyacinth, crop residues, forest litter, etc. research work is in progress to develop suitable designs of biogas plants.

1.3 Biogas Plants:

There are three tested and field-worthy designs of biogas units[20]. The names of these three models are given below:

i) Floating gas holder type (Gobar gas plant),

ii) Fixed dome type (Janata biogas plant), and

iii) Ganesh model

1.3.1 Floating gas holder type:

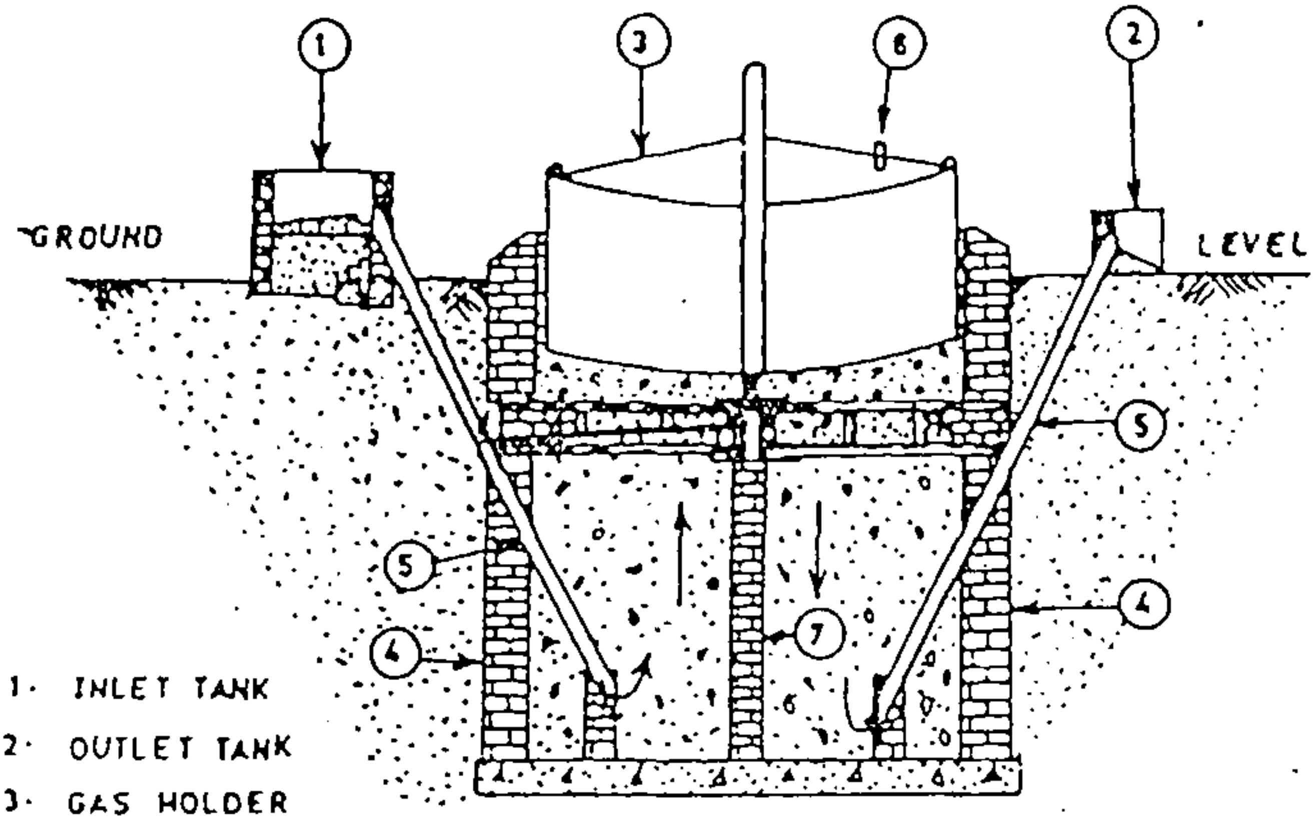
This design was first developed in India in 1954 and the Khadi and Village Industries Commission (KVIC), Bombay, adopted it for promotion in 1962. Therefore, it is also known as KVIC type gobar gas plant.

There are two models of floating gas holder type biogas plants:

a) Vertical model,

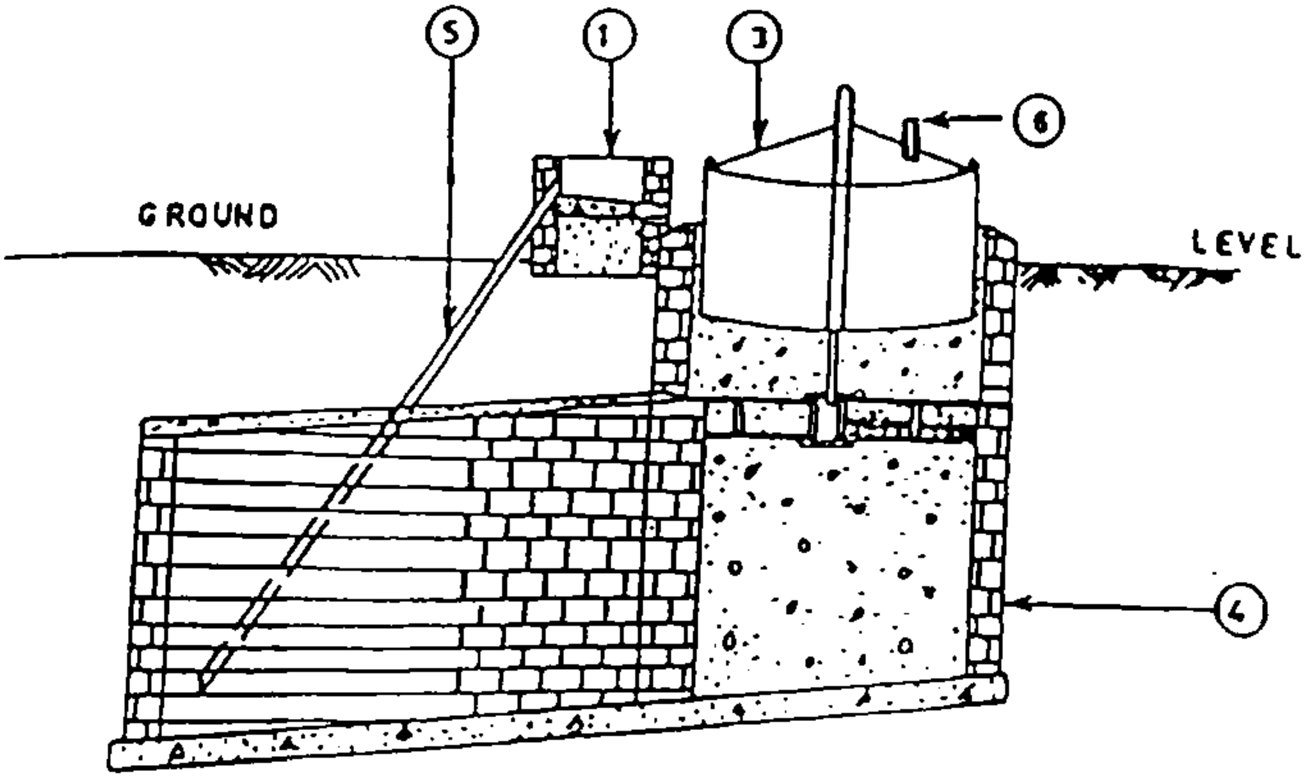
b) Horizontal model.

The vertical model (Fig. 1.2) is suitable for non-rocky areas with a low water table. The horizontal model (Fig. 1.3) is recommended for rocky areas with high water tables. Design specifications have been standardised for both these models for average biogas production capacities ranging from 1 to 85 cubic metres.



1. INLET TANK
2. OUTLET TANK
3. GAS HOLDER
4. DIGESTER WALL
5. A.C.PIPES
6. GAS OUTLET
7. PARTITION WALL

Fig. 1.2 : Vertical floating gas holder type biogas plant



1. INLET TANK
2. OUTLET TANK
3. GAS HOLDER
4. DIGESTER WALL
5. A.C. PIPES
6. GAS OUTLET
7. PARTITION WALL

Fig.1.3 : Horizontal floating gas holder type biogas plant

The floating gas holder type biogas unit consists of i) digester ii) gas holder iii) inlet and outlet assembly, and iv) water removal device.

The feedstock is collected and mixed with water in a mixing tank which is a part of the inlet assembly. The feedstock slurry is allowed to enter the digester through an inlet pipe made of asbestos cement. The slurry is retained in the digester for a certain period of time (30,40 or 55 days as per recommendations for different areas) for decomposition. The diameter and depth of the digester vary according to the capaicty of the unit. The digester has a partition wall in the middle, dividing it into equal halves. The slanting pipes reach the bottom of the digester on either side of the partition wall and open out on the surface of the foundation of the digester. One pipe serves as an inlet and the other as an outlet.

The gas holder assembly consists of a central guide frame, a drum made of mild steel sheet and a gas outlet. The drum is kept upside down on the digester so that it dips in the slurry and rests on a ledge constructed inside the digester. It collects gas which comes out of the slurry and moves up. When the gas outlet is opened, the gas so collected is pushed out into the pipeline by the weight of the drum itself, at a constant pressure of 8-10 cm. water column. The drum then moves down. This up and down movement of the drum is guided by a central guide pipe fitted in a frame which is fixed to the digester wall.

1.3.2 Fixed-dome type (Janta Biogas Plant):

This was first developed by the State Planning Institute, Lucknow in 1978. It is an improved version of the Chinese Fixed-dome biogas plant.

The fixed-dome type biogas unit (Fig. 1.4) is entirely a masonry structure. It dispenses with the use of a steel gas holder. Both the digester and the gas holder form an underground combined unit. The dimensions of the inlet and outlet are bigger than those of the floating gas holder type biogas units. Other parts, namely, gas outlet and pipeline assembly are common in both types of plants.

The feedstock slurry is allowed to ferment in the digester. When gas is formed, it rises upwards and gets collected in the dome. The pressure of the gas pushes the slurry down and causes its diffusion into the inlet and outlet chambers where slurry levels go up. The displaced level of the slurry provides the necessary pressure pushing the gas up to the burner in the kitchen.

The gas is liberated at a variable pressure ranging from 0 to 99 cm of water column. When gas is consumed, the slurry level in the inlet and outlet chambers comes down to the initial level. The volume of the gas stored in the plant at any given time is equal to the total volume of slurry displaced in the inlet and outlet chambers.

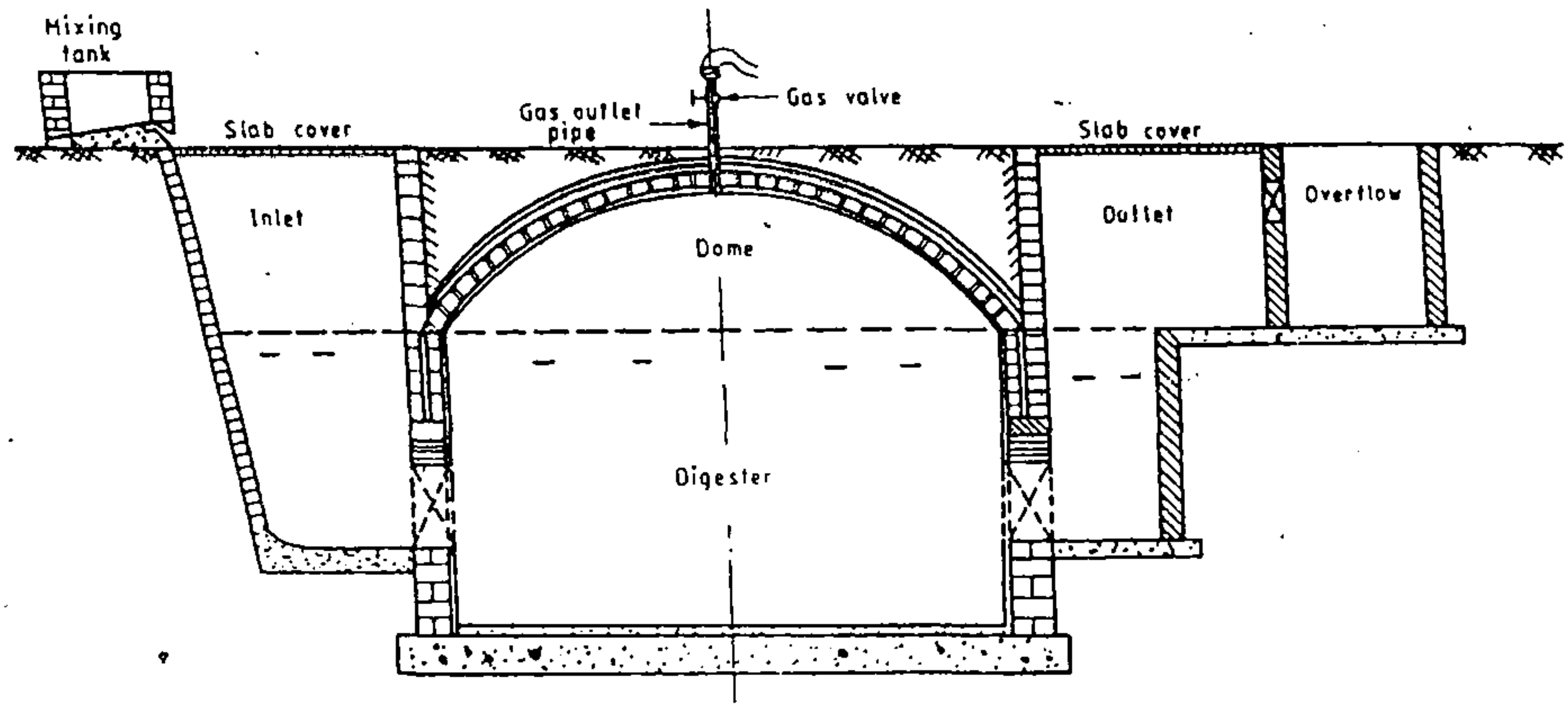


Fig 1.4 : Fixed -dome type biogas plant

The gas is liberated at a variable pressure ranging from 0 to 99 cm of water column. When gas is consumed, the slurry level in the inlet and outlet chambers comes down to the initial level. The volume of the gas stored in the plant at any given time is equal to the total volume of slurry displaced in the inlet and outlet chambers.

It should be noted that the diameter and height ratio of the digester is fixed at 1.75:1. The height of the portion above the inlet and outlet openings is so fixed that the volume of this portion is equal to the total maximum volume of gas to be stored in the plant and the volume of slurry to be discharged everyday. The volume of the dome is 60% of the plant capacity. The plant should be constructed underground as per the recommended specification in order to get the rated gas production.

1.3.3 Ganesh Model:

It is an adapted version of the floating gas holder type design with the exception that the digester portion is made of an angle iron frame wrapped in a polythene sheet instead of the masonry structure (Fig. 1.5). The cost of installation of the digester is about 30-40% less. It is easy to transport materials required for fabrication of the digester and less time is taken to install it.

1.4 Effect of various parameters on the biogas production:

The anaerobic process is in many ways ideal for waste treatment. It has several significant advantages over other available methods and is assured of increased usage in the

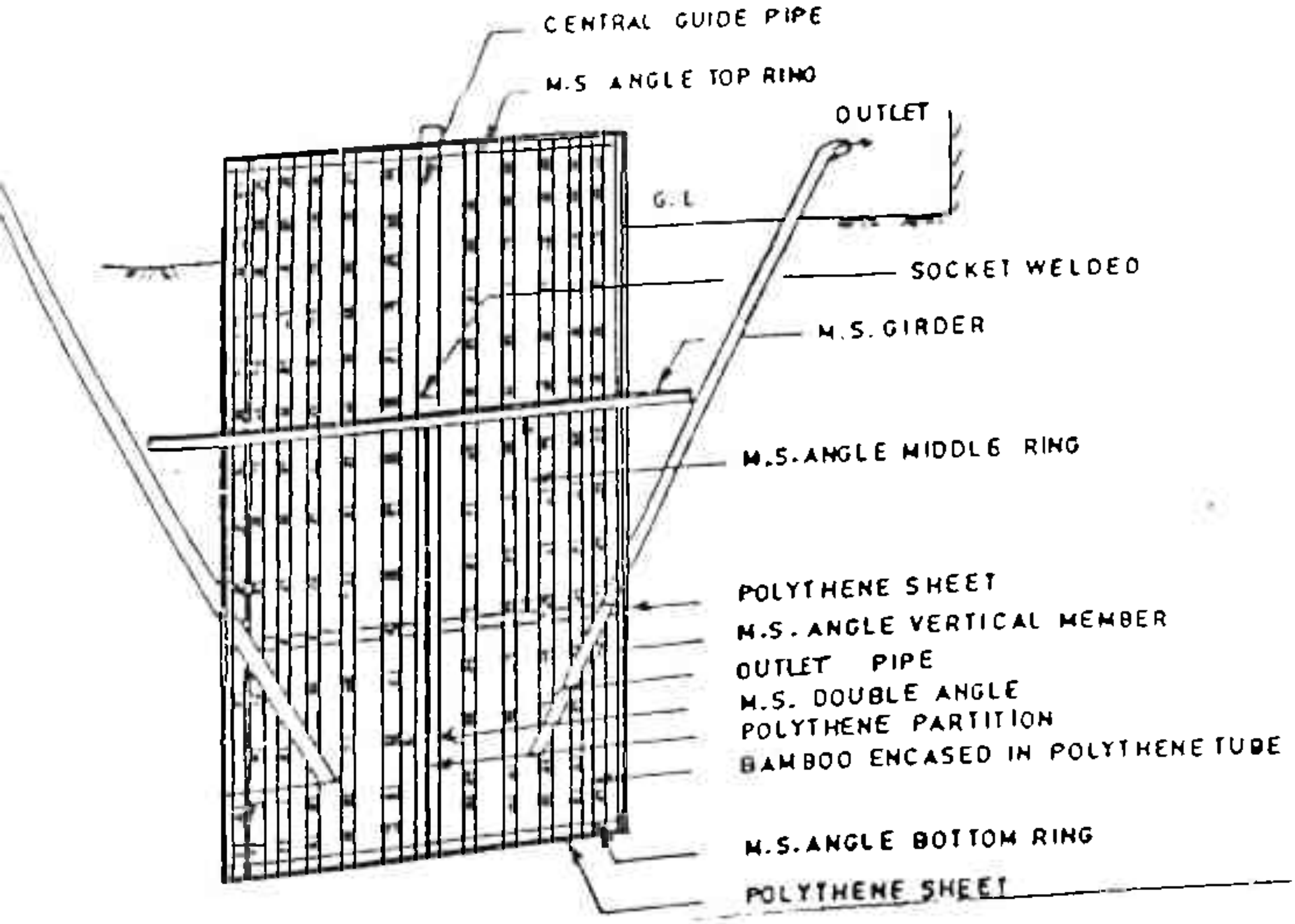


Fig.1.5: Ganesh model of biogas plant

future. However, in spite of its present significance and a large future potential of this process, it has not generally enjoyed the favourable reputation it truly deserves. Digesters are also susceptable to malfunctioning due to shock of loading, temperature, etc. Under normal running condition, anaerobic waste treatment proceeds with a minimum control. However, if environmental conditions are changed, or if toxic materials are introduced, the process may become unbalanced. An "unbalanced process' is defined as the one which is operating at a less than normal efficiency.

The quantity of biogas production from the biomass depends mainly on the temperature of fermentation, and retention time. Besides these, many other factors like agitation, total solid content and pH affect gas production. It was felt, therefore, necessary to find out the optimum conditions in terms of i) temperature ii) retention time iii) agitation iv) total solid content, and v) pH for maximum gas production [8].

1.4.1 Temperature:

Biogas production greatly depends on temperature [9]. The optimum temperature range is 30-40°C. During winter season, with a drop in the temperature, the production of gas also drops. In such a situation, the following tips may be useful.

i) Warm water can be used for dilution of feedstock. For this a solar heating system could be used.

ii) Diluted feedstock slurry can be prepared in the mixing tank and kept for the whole day to warm up. Then the digester may be loaded in the evening.

iii) An addition of organic matter containing a higher percentage of nitrogen like urine, nightsoil, etc. increases the gas production.

iv) The gas holder should be kept covered with plastic sheets or gunny bags during the night so that it remains insulated and heat loss is minimised.

v) A tent made of plastic sheet can be erected over the biogas plant. This gives a green house effect provided the joints are made air-tight. It may increase gas production by 50-60%.

1.4.2 Retention time:

It is the period for which slurry should be held in the digester for getting 80% of the total gas. At low retention time, the percentage of methane in the product gas will be more. The effect of temperature on the rate of gas production is more apparent after a short time rather than after a long retention time[31].

Plants based on 30 days Retention period:

These are recommended for Andaman and Nicobar Islands, Andhra Pradesh, Goa, Karnataka, Kerala, Maharastra, Pondichery and Tamilnadu.

Plants based on 40 days Retention Period:

Such plants are recommended for Bihar, Gujarat, Haryana, Jammu area of J & K State, Madhya Pradesh, Orissa, Punjab, Rajasthan, Uttar Pradesh and West Bengal.

Plants based on 55 days Retention period:

These are recommended for Himachal Pradesh, all North- Eastern Regional states, Sikkim, hill districts of Uttar Pradesh and such areas that have severe winter for long periods.

1.4.3 Agitation:

The stirring is required for higher amount of biogas production. Stirring time varies from 25 to 30 minutes per day. It is done for uniform mixing of the slurry and hence to increase the growth of the population of the microorganism. Agitation can be done by a magnetic stirrer. Occasional stirring improves the amount of total gas production. Continuous stirring allows scum formation on the fermentation mixture resulting in the decrease in biogas production, whereas occasional stirring improved volatile acid concentration as well as increased rate of bio- degradation.

1.4.4 Total solid content:

The quantity of biogas production depends on the total solid content in the feedstock. The total solid content in the range of 7.5 to 10 per cent is found to be most suitable for giving better results in terms of total gas production and methane content.

1.4.5 The pH value:

pH is considered to be one of the most important parameters in maintaining the efficiency of anaerobic fermentation. Maximum efficiency in fermentation is obtainable near neutral pH (between 6 and 8). Generally in the anaerobic process, high volatile acid concentration accounts for a decrease in pH value.

1.5 Biogas production from different waste materials - case studies

This section presents an overall picture of past efforts made for the production of biogas from different waste materials.

As early as in 1969, Shirley discovered marsh gas [11]. It was the discovery that gases emitted from water-inundated marshlands were combustible which led to the theory and current practice of gas energy recovery from the decomposition of organic materials in liquid and oxygen free environment.

On November 14, 1776 Alessandro Volta [11] wrote a letter to a friend describing his unexpected discovery that 'combustible air' was being formed continuously and in sub stantial quantities in all the lakes, ponds and streams in the vicinity of Como in northern Italy. The initial observation was made in Lake Verbano. Chemical knowledge of those days did not permit the characterization of Volta's inflammable gas. This was first accomplished in 1806 by William Henry [11], who showed that Volta's gas was apparently identical with the main constituent of synthetic illuminating gas which was later called methane. In 1808, Humphry Davy [11] collected the gas from the decomposition of straw, cattle, manure, and thus began the biogas research.

In the year 1868, Bechamp, a pupil of Louis Pasteur, clearly showed that methane is perhaps formed from simple carbon compounds by action of microorganisms and subsequently more adequate proof of the microbiological origin of methane was provided by Tappeiner in 1882-1884 [16]. It was only a few years later, in 1896, that sewage gas was used for lighting a street in Exeter, England [11].

India took the lead in the development of biogas plants (locally known as gobar-gas plants). The Indian Council of Agricultural Research (ICAR) had begun anaerobic cow-dung fermentation as early as 1938-39 [9]. In 1956, the government started setting up biogas plants on a large scale. In 1960's the 'Khadi and Village Industries Commission' took keen interest in the setting up of biogas plants in villages. It provided financial assistance and free technical know-how for this purpose. Nearly 70% of India's biogas plants, which now total more than 50,000 were built during the fuel and fertilizer crisis of 1975-76. Currently, in India a number of agencies are involved in the development and propagation of biogas technology.

Nearly 27,000 small digesters have been installed in The Republic of Korea since 1969 through the efforts of the office of Rural Development. However, the cold winters and lack of cattle make Korea's experience with biogas quite different from that of India. Most farmers do not operate the digesters between December and March, when temperatures are as low as -17°C, and gas production is almost nil.

Fuel is not a major problem in the Philippines as fire-wood is plentiful. Consequently, interest in biogas stems from its concern for pollution control and maintenance of public health . Pigs and buffaloes provide most of the animal wastes, and despite some psychological inhibitions the National Housing Authority(NHA) is also promoting night-soil digestion, and one such digester is already operational. The major research activity is centered at the National Institute of Science and Technology (NIST), at the University of Philippnes at Los Banos and Maya Farms[12].

In countries like Thailand and Indonesia, not much development of biogas technology has taken place since firewood is plentiful in most areas and animal waste is not so plentiful [12].

In Japan, several institutions, including the National Institute of Animal Industry at Chiba, the Public Works Research Institute, the Fermentation Research Institute at Anage, M/S Hitachi Plant construction, the Ministry of Agriculture, and the Agency of Industrial Science and Technology (MITI) have worked on anaerobic digestion of rural, urban, and industrial waste for pollution control. They have adopted high temperature digester in the thermophillic range of some wastes[16].

In China, biogas is extensively used for cooking, lighting, making fertilizer, and for running small internal combustion engines [5].

Klass presented a general view of the status of research and technology on the conversion of wastes and biomass into various forms of usable energy [25].

Clausen et al. [21] reviewed various aspects of methane production from crop materials including sources of biomass in relation to crops and available land, kinetics of bio-methanation, process description, and overall system economics.

Chiranjivi [26] revised various methods of construction and operation of biogas units. Most of these units were on a small - scale, at a low- cost and based on simple operating procedures at ambient temperatures.

An experiment was conducted, by Boopathy R., with coffee pulp and cow-dung in order to find out the biochemical and microbiological mechanism involved in CH_4 production [39].

Rajsekaran et.al. conducted experiments with Euphorbia leaves and cattle manure to study the biogas production potential [45].

An experiment was conducted by Shinnawi M. M., et al. [28] to find out the change in organic constituents of crop residues and poultry wastes during fermentation for biogas production. Rice straw, maize, and cotton stalks and poultry droppings, with either wheat straw litter or sawdust litter were used as substrate for biogasification.

M.H. Wong, et al. reported [29] that pig manure with either saw dust or cardboard (4:1) especially saw dust, could produce higher total volume of biogas than with newspaper or sugar cane waste.

R. Sarada et al. reported [39] that a high yield of total gas and methane were obtained at 24 day HRT and 4.5 kg/m^3 loading rate and at 35°C.

Rohella, R.S. et al. reported that with the particle size reduction, alkali pretreatment of feedstock, the addition of nutrients (C,N and P) and pH buffer, the biogas generation from the agro-waste could be enhanced from 35 to 131 litres/kg of total solid added in the digester [46].

A universal basic model of anaerobic conversion of complex organic materials has been suggested by V.A. Vaviline, et al. The model can be used for investigating the start-up experiments for food industry waste water [31].

Harpal Singh et al. reported [36] the critical effect of soil to water ratio, hydraulic retention time and the use of additives and simulants on biogas production .

G.P. Nagori, et al. reported [37] the methane production from effulents from caseien and ghee sections of a dairy from the up flow anaerobic fillet reactor . They fabricated two anaerobic filter reactors using PVC pipes and fittings. The reactors were operated over a range of HRT(hydraulic retention time) and organic loading rates. The reactor performance was deter mined in terms of COD reduction and methane production.

Anjan K. Kalia et al. reported [38], the biogas generation from Ageratum in semi - continuous plants. According to them the mixture of partially aerobically decomposed chopped Ageratum and cattle - dung in the ratio of 3:2 can produce biogas with higher methane content than that obtained from pure cattle - dung.

Sharma Archana reported [47] the inhibitory effects of litrous unshiu- peel on anaerobic digestion. The inhibitory effect on biogas production was mainly due to peel oil.

Dhawale M.R. et al. reported [40] the methods of maximizing biogas production from cattle-dung in anaerobic digester. They have found out the optimum values of retention time and total solid content for which maximum biogas can be generated from the cow-dung.

Ranade D.R. et al. reported [48] that biogas production from the cow-dung depends on the total solid content in it. Experiments have been conducted of find variation of biogas production from cow-dung with the solid content in it.

Nynes E. J. reported [34] that biogas production can be improved by adding some metal ions in the slurry of the organic wastes.

Lawrence A. W., Mc Carty P.L. reported [33] the simulative effects of some metal ions on biogas production from the organic wastes when added in low concentration, but they are toxic at higher concentration.

1.6 Plan of work

From the literature survey (Chapter-1), it has been found that there is hardly any published work on the comparative study of biogas production from different waste materials. There are a large number of locally available waste materials such as different kinds of waste-flowers, kitchen-wastes, leaves and vegetables for which no reports have been published. It was therefore planned to select some of these waste materials which had not been selected so far, to make a comparative study for finding out the relative biogas generation capacity of each of them through the process of anaerobic digestion.

Chapter-2 describes the experimental set up used for the biogas production including the experimental procedure and the analysis of the substrate sample and the product gas. A comparative study of biogas production from the mixtures of cow-dung and the kitchen-wastes forms Chapter-3. The mixture of cow-dung and another kind of waste material, namely, waste flowers are used for biogas production. This comparative study is given in Chapter-4. A third comparative study of biogas production from the mixtures of cow-dung and waste leaves and vegetables forms Chapter-5. It has also been observed from the literature survey that several reports [32-35] have been published on the effect of some metal ions, additives etc., on the biogas production. However, there is hardly any report on the effect of metallic catalysts on biogas generation. So it was decided to perform some experiments by selecting a number of metallic catalysts. Chapter-6 is used to explain the above experiments.

CHAPTER - 2

LABORATORY SCALE EXPERIMENTAL SET UP OF AN ANAEROBIC DIGESTIVE SYSTEM AND ANALYSIS OF THE SUBSTRATE SAMPLES AND THE PRODUCT GAS

Chapter-2

Laboratory scale experimental set up of an anaerobic digestive system and analysis of the substrate samples and the product gas

In this Chapter, an attempt has been made to study the functions of the different parts and accessories of a laboratory scale experimental set up of anaerobic digestive system. Efforts have also been made to explain the experimental procedure of biogas production in an anaerobic digester, and the analysis of the sample substrate and the product gas.

2.1 Laboratory scale experimental set up of an anaerobic digestive system:

The bench scale experimental set up (Fig. 2.1) consists of the following major components:

i) Digester

ii) Gas collector

iii) Magnetic stirrer

iv) Thermostat:

a) Relay

b) Contact thermometer

c) Fan

d) Electric bulb

e) Enclosure

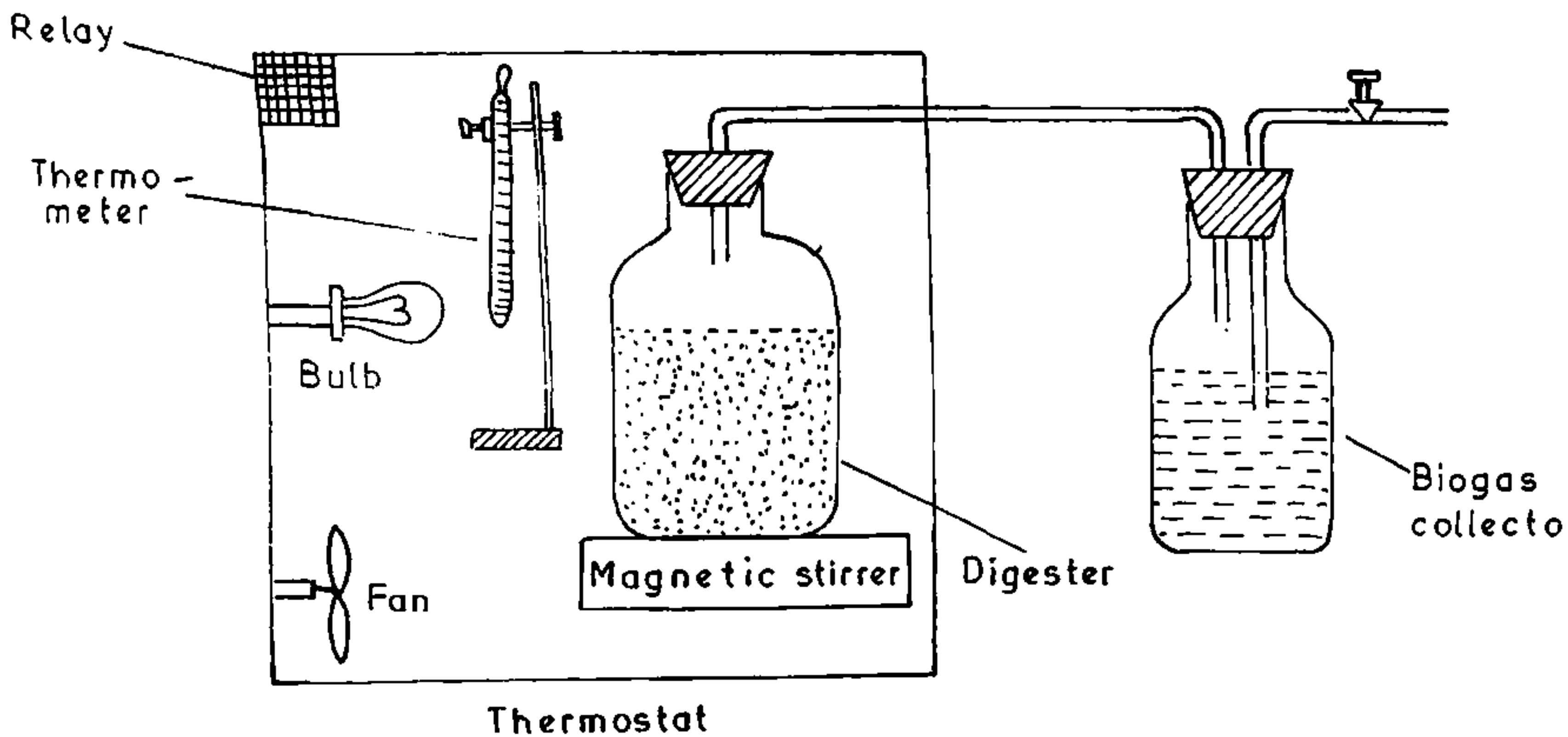


Fig 2.1.8 Laboratory scale experimental setup of an anaerobic digestive system.

2.1.1 Digester:

Several bench scale anaerobic digesters were used. Each digester is a 500 c.c conical flux containing 300 c.c slurry of the waste materials to be digested for biogas production. It was essentially a biogas generator.

2.1.2 Gas Collector:

This was used to collect the biogas generated by the digester. Each gas collector consisted of a 2 litre capacity bottle, containing acidified water. The gas was collected and measured by the displacement of acidified water (30 ml concentrated H_2SO_4 per 1 litre of water).

2.1.3 Magnetic stirrer:

The objective of using this was to agitate the digester. Stirring was required to make uniform mixing of total solid and spreading of micro-organism in the digester. Stirring time varied from 25 to 30 minutes per day.

2.1.4 Thermostat:

It was used to maintain the desired temperature of digester for maximum gas production. All digesters were maintained at 37°C ± 1°C in a thermostat. The thermostat consisted of the following components:

i) Relay: A contact relay was used to switch on and off the temperature controlling devices of the thermostat.

ii) Contact thermometer: It was used to read the temperature of the thermostat to be set at the desired level.

iii) Fan: The fan was used to circulate air inside the thermostat to make uniform temperature at each point of the thermostat. The fan was used for 24 hours at low speed.

iv) Electric Bulb: Two electric bulbs, 200W each, were used in each thermostat. The temperature of the each digester was maintained at 37°C using heat delivered by the bulbs. The bulbs started glowing when the temperature of the thermostat fell below the above temperature and the bulbs were off when the temperature of the thermostat reached the above desired level. The 'Off' and 'On' positions of the bulbs were controlled by the contact relay.

v) Enclosure:

All the above mentioned components of the thermostat were placed inside a cubical enclosure made of cardboard.

2.2 Selection of raw materials for biogas production:

There are various types of waste materials available in our country. But all waste materials are not feasible for biogas generation. Only biodegradable waste materials (biomass) can produce biogas [42]. Again, the biogas generation capacity is not same for all waste materials. It depends on the total solid, volatile solid, suspended solid contained in the waste materials and Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) values of the same.

Some of the waste materials, particularly agro-wastes, are not biodegradable due to the presence of lignin. To make these waste materials biodegradable, pre-treatment is required to remove lignin so that they can be used for biogas generation.

Some of the raw materials, that can be used for biogas generation, have been mentioned in the Section 1.5, Chapter-1 (Case studies). Locally available waste materials, which were not used by the previous investigators for biogas generation, have been selected for this investigation. Fermentation of cattle-dung offers several advantages over other substrates. Adequate nutrients are available in the above raw material for the microbes to carry out fermentation. So the mixtures of cow-dung and other raw materials have also been considered for biogas generation.

Raw materials, which were selected for conducting some experiments on the anaerobic digested system, were as follows:

i) Cow-dung

ii) Kitchen - wastes

iii) Waste flowers

iv) Waste leaves and vegetables.

2.3 Experimental Procedure:

Experiments were conducted to make the comparison between the biogas generated by the fresh slurry of cow-dung alone and the biogas generated by the mixture of cow-dung and the various waste materials. Experiments were also conducted to study the effect of different metallic catalysts on the biogas generation.

A 500 c.c. glass bottle was used as a digester in each treatment/set and the slurry containing the mixture of cow-dung, waste material and water in the ratio of 1:1:2 by weight, was poured into these in the beginning of the experiment. Each digester was connected through a plastic tube to another glass bottle filled with acidified water.

The digesters were kept inside the thermostat for 90 days and the amount of biogas produced was measured daily. The biogas was analyzed once in a week to find out the percentage of methane.

2.4 Analysis of the substrate samples and the product gas using standard procedures :

Substrate samples were routinely analyzed for pH, BOD, COD, DO, total solid and Volatile Solid (VS) and the product gas as follows:

2.4.1 Determination of pH:

pH was measured by Beckman pH meter [44]. At first, it was standardized by dipping the pH probe into buffer solution having pH 7.0. Then it was dipped into the sample for which pH was required to be determined.

2.4.2 DO (Dissolved oxygen) test :

To determine DO the sodium azide, a modification of the Winkler method [23] was used.

For this , 2 ml $MnSO_4$ solution (364 g of $MnSO_4$, H_2O in 1 litre of water) was added to a 300 ml diluted sample, followed by an addition of 2 ml alkali-iodide reagent (500 g NaOH, 135 g NaI and 10 g NaN_3 in 1 litre water) below the surface in a stoppered BOD bottle and mixed by inverting it. 2 ml con. H_2SO_4 was added to this solution. The contents were mixed by gently inverting until the dissolution of the brown precipitate was completed. 50 ml of sample was removed and titrated with thiosulphate.

The following formula was used to calculate DO:

$$\text{mg/litre DO} = \frac{\text{ml. of } Na_2S_2O_3 \text{ x Normality of } Na_2S_2O_3 \text{ x } 8000}{50 \text{ ml of sample titrated}} \qquad (2.1)$$

2.4.3 BOD (Biochemical oxygen demand) Test:

The BOD [23] by definition, is the quantity of oxygen required for the stabilization of oxidizable organic material present after 5 days of incubation at 20°C. In most cases, complete stabilization, would take a much longer time. The degree of oxidation occurring during a 5-day period depends on the type of micro-organisms present in the waste material and the type of nutrients and temperature.

Dilution water was made for BOD experiment. 1.0 ml each of phosphate buffer (8.5 g KH_2PO_4, 21.75 g K_2HPO_4 33.4 g Na_2HPO_4, $7H_2O$, 1.7 g NH_4Cl in a 1 litre of distilled water), magnesium sulphate solution (22.5 g $MgSO_4$, $7H_2O$ in a 1 litre of distilled water), calcium chloride solution (27.5 g of anhydrous $CaCl_2$ in 1 litre of water), and ferric chloride solution (0.25 g of $FeCl_3$, 6 H_2O in 1 litre of water) were added for each litre of water. The buffer was used to maintain the pH of 7.2 of the solution Magnesium calcium and ferric ions were used as nutrients for the growth of bacteria.

The measured samples were added directly to two BOD bottles (300 ml capacity) and filled with just sufficient dilution water so that the stopper could be inserted without leaving air bubbles. One bottle was incubated for 5 days at 20 C temperature.

For calculating BOD, the following formula was used:

$$BOD\ (mg./litre) = \frac{(D_0 - D_5)}{P} \qquad (2.2)$$

Where, D_0 = DO of diluted sample 15 min. after preparation.

D_5 = Do of diluted sample after incubation

P = Decimal fraction of sample used

$$= \frac{\text{Volume of the sample}}{300\ ml}$$

Chemical reactions involved in DO-BOD tests:

$MnSO_4 \rightleftharpoons Mn^{+2} + SO_4^{-2}$

Alkaline KI $\rightleftharpoons K^+ + I + OH^-$

$Mn^{+2} + 2OH^- + 1/2\ O_2 \rightarrow H_2O + MnO_2$ brown precipitate

Brown precipitate indicates presence of oxygen. In the absence of oxygen $Mn(OH)_2$ is precipitated out as white precipitate

$Mn^{+2} + 2OH^- \rightarrow Mn(OH)_2$ white precipitate

$MnO_2 + 4H^+ + 2I^- \rightarrow I_2\ (gas) + Mn^{+2} + 2H_2O$

Starch + $I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2Na\ I$ (colourless)

(Blue colour)

2.4.4 COD (Chemical Oxygen Demand) Test:

The acid-dichromate reflux method [23] was used for the COD determination because it has an advantage over other oxidants in oxidizability. The chemical oxygen demand (COD) determination provides a measure of the oxygen equivalent of that portion of the organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant.

A standard COD determination gives higher oxygen demand than a 5 day BOD determination since the oxidation of organic material is almost complete. The COD test is explained below:

10 ml. of suitably diluted sample was taken in the first flask. 10 ml of distilled water was taken in the second flask. 5 ml of 0.25 (N) potassium dichromate (12.259 g $K_2Cr_2O_7$ in 1 litre distilled water) solution and 15 ml concentrated sulphuric acid (75 c.c. H_2SO_4 contains 1 g Ag_2SO_4 catalyst) were added to each flask. Contents of the flasks were mixed with gentle shaking and refluxed for 1 hour. Each flask was cooled and the final volume of the solution was made upto 70 ml by adding distilled water. The excess dichromate was determined by titrating with standard ferrous ammonium sulphate solution [0.10(N) $FeSO_4$, $(NH_4)_2SO_4$ solution : 39 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ was dissolved in distilled water. 20 ml concentrated H_2SO_4 was added, cooled and diluted to 1000 ml.] This solution was standardised against the standard potassium dichromate solution using 2-3 drops (0.10 - 0.15 ml) of ferroin indicator. At the end point colour changes from bluish-green to reddish brown. COD was calculated as below :

$$\text{COD(mg/l)} = \frac{(A-B) \times N \times 8000}{D \times E} \qquad (2.3)$$

Where,

A = ml $Fe(NH_4)_2(SO_4)_2$ used for blank

B = ml $Fe(NH_4)_2(SO_4)_2$ used for sample

N = Normality of $Fe(NH_4)_2(SO_4)_2$ solution

D = ml of solution after reflux used for titration

E = dilution factor = Vol. of sample / 10 c.c.

2.4.5 Determination of total solid (TS):

The total solid content was determined [23] by taking the measured volume of samples into the weighed crucibles and heated in a constant temperature oven at 105 C for 5 hours. The crucibles were cooled and the weight of the residue was determined.

The calculation was done according to the formula given below:

$$\text{Total solid (mg/l)} = \frac{(W_2 - W_1) \times 1000}{V} \quad (2\cdot4)$$

Where,

W_1 = Weight of empty crucible

W_2 = weight of crucible + residue

V = ml sample used

2.4.6 Determination of volatile solid (VS):

To determine the volatile solid [23] present in the sample of the residue obtained (which had been earlier heated at 105°C in the oven) was reheated at 600°C for 5 hours in a furnace.

After cooling the residue its weight was taken.

Calculation for volatie solid was done according to the formula:

$$\text{Volatile solid(mg/l)} = \frac{(W_2 - W_1) - (W_3 - W_1) \times 100}{V} \tag{2.5}$$

$$= \frac{(W_2 - W_3) \times 100}{V}$$

$$= \frac{(\text{Total solid - ash}) \times 100}{\text{vol. of sample}}$$

Where,

W_1 = weight of empty crucible (mg)

W_2 = weight of crucible + residue obtained at 105°C

W_3 = weight of crucible + residue (ash) obtained at 600°C

V = ml sample used

Residue obtained at 600 C is called ash.

2.4.7 Analysis of biogas using the Orsat apparatus [43]:

The simple Orsat apparatus (Fig. 2.2), was employed to analyze the product gas obtained from the anaerobic digester. It consisted of a measuring burette and three pipettes

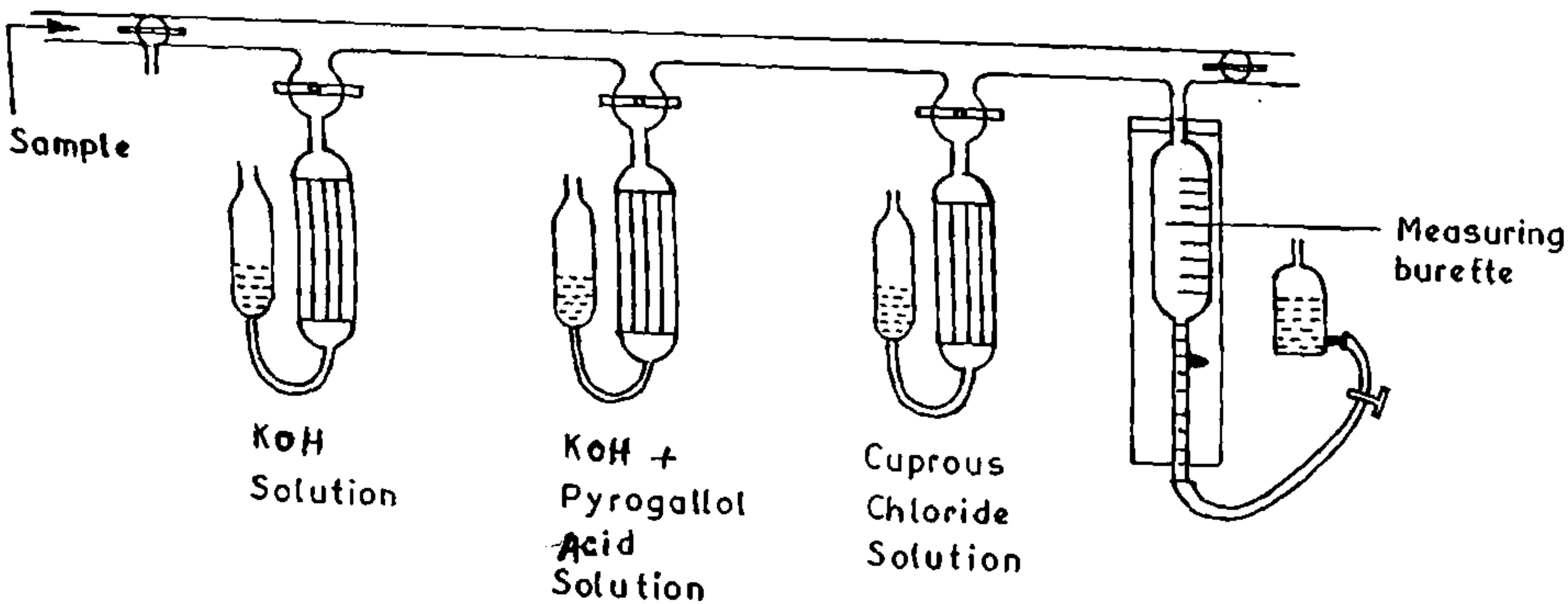


Fig. 2.2 Schematic diagram of the Orsat apparatus

which were used to successively absorb carbon dioxide, oxygen and carbon monoxide from the mixture.

First, a sample of the product gas was drawn into the measuring burette. Next, the sampling manifold was shut off and the sample was forced into the first reagent pipette, containing potassium hydroxide (KOH 30 g in 100 c.c)(2) solution, where carbon dioxide was absorbed. The sample was then brought back into the measuring burette, and the reduction in volume was noted. The procedure was then repeated for another pipette, where O_2 was absorbed. O_2 was absorbed by alkaline potassium pyrogallate solution. The third pipette contained ammonical cuprous chloride solution. This solution was used to absorb carbon monoxide. Biogas contained no carbon monoxide, the volume of CO was zero. In the measuring process the product gas was collected over acidified water (5% H_2SO_4 solution) in the burette.

Calculations were done as below:

Let V = volume of the gas sample (c.c.)

V_1 = volume of CO_2 absorbed in KOH solution (c.c.)

V_2 = volume of the O_2 absorbed by the alkaline potassium pyrogallate solution (c.c.)

Volume of $(CH_4 + N_2 + O_2) = V - V_1$ (c.c.)

Volume of $(CH_4 + N_2) = V - V_1 - V_2$ (c.c.)

Volume of $N_2 = (79 \times V_2) / 21 = V_3$ c.c.

(Composition of air : 79% N_2 and 21% O_2 by volume)

Volume of $CH_4 = V - V_1 - V_2 - V_3$ (c.c.)

$$\% \text{ of } CH_4 = \frac{(V - V_1 - V_2 - V_3) \times 100}{V}$$

$$\% \text{ of } CO_2 = \frac{V_1 \times 100}{V}$$

CHAPTER - 3

A COMPARATIVE STUDY OF BIOGAS PRODUCTION FROM THE MIXTURES OF COW-DUNG AND KITCHEN-WASTES

CHAPTER - 3

A comparative study of biogas production from the mixtures of cow-dung and kitchen-wastes

A large amount of kitchen-wastes like potato-peels banana-peels, orange peels, tea-leaves, different fruit-peels, etc, are available from the hotels, restaurants, domestic kitchens, etc, everyday. When these waste materials are dumped on the earth, they create pollution and at the same time the energy of these waste materials is unutilized. But it is possible to produce biogas when the mixtures of these waste materials and cow-dung are utilized in the anaerobic digesters and the energy is extracted from these waste materials.

In this Chapter, an effort has been made to present the results of some experiments conducted on the laboratory scale anaerobic digesters to make a comparative study of biogas production from the mixtures of cow-dung and some kitchen-wastes as raw materials for biogas production. The kitchen-wastes which were selected for the above experiments were:-

i) Tea-leaves

ii) Banana-peels

iii) Orange-peels

iv) Potato-peels

3.1 Experiments:

To conduct some experiments for the production of biogas from the kitchen-wastes, one sample containing the slurry of cow-dung and four samples containg the slurry of the mixture of cow-dung and different kitchen-wastes were used. The above five samples were as follows :

Sample-1: The mixture of cow-dung and water (1:1)

Sample-2: The mixture of cow-dung, tea-leaves and water (1:1:2)

Sample-3: The mixture of cow-dung, banana-peels and water (1:1:2)

Sample-4: The mixture of cow-dung, orange-peels and water (1:1:2)

Sample-5: The mixture of cow-dung potato-peels and water (1:1:2)

Preparation of the samples:

The general procedure of preparing each of the above samples was as follows:

To prepare Sample-1, 200 g of cow-dung was mixed with 200 g of water in a flask and shaken well. For preparing the other four samples, at first each kitchen-waste was grinded to make a paste. 100 g of paste was mixed with equal amount of cow-dung. 200 g of water was added to the each of these mixtures of cow-dung and kitchen-waste to make a slurry.

The following tests were conducted for the each of the above samples:

i) Determination of COD, BOD, VS and pH of the samples.

ii) Determination of total amount of biogas produced by the samples in the anaerobic digesters.

iii) Determination of methane content in the biogas produced by the samples using the Orsat appartus.

3.1.1 Determination of COD, BOD, VS and pH of the samples:

To find out the bio-degradability of the samples and thereby predict the biogas generation capacity, COD, BOD, VS and pH were determined for each sample. A part of the prepared slurry of each sample was taken for the above purpose. Each sample was tested to determine above paramters, using standard methods as described in Chapter-II. The test results have been shown in Table 3.1.

TABLE 3.1

COD, BOD,VS and pH of each of the samples of the kitchen wastes

Sample	COD (mg/l)	BOD (mg/l)	VS (mg/l)	pH
1. Cow-dung +water	6737	4624	5500	6.4
2. Cow-dung +tea-leaves+ Water	6825	4630	5592	6.4
3. Cow-dung+ banana-peels +Water	7824	5500	6825	6.4
4. Cow-dung+ orange peels +water	6682	4000	4656	6.35
5. Cow-dung+ potato peels +water	7720	5000	6655	6.4

3.1.2 Determination of total amount of biogas produced by the samples in the anaerobic digesters:

To study the biogas generation capacity of each sample consisting of 300 c.c slurry, each of the five samples was poured separately into five 500 c.c bottles which were used to act as the anaerobic digesters. All the five digesters were kept inside a thermostat for 90 days. The temperature inside the thermostat was kept at a constant temperature of 37 °C ± 1°C. Each digester was agitated 5 to 6 times daily, with the help of a magnetic stirrer to spread the population of bacteria in all parts of the slurry. The biogas produced by each sample was collected by the displacement of acidified water in a graduated measuring bottle. The amount of biogas generated by each sample was measured daily and thus the total amount of biogas produced by each sample in 90 days was determined. The results have been shown in the Table 3.2.

3.1.3 Determination of methane content in the biogas, produced by the samples, using the Orsat appartus:

The biogas generated by each sample was analysed once in a week to determine the methane content in it. This analysis was done using the Orsat apparatus. Thus the variation of the methane content in the biogas genrated in 90 days was found out.

TABLE - 3.2

Total amount of biogas generated by each of the samples of the kitchen-wastes

Total volume of the slurry in each digester = 300 c.c

Composition of the sample	Retention time (days)	Total amount of biogas generated(c.c)
Sample-1: Cow-dung and water (1:1)	90	1500
Sample-2: Cow-dung, tea-leaves and water (1:1:2)	90	1600
Sample-3: Cow-dung, banana-peels and water (1:1:2)	90	3000
Sample-4: Cow-dung, orange-peels and water (1:1:2)	90	400
Sample-5: Cow-dung, potato-peels and water (1:1:2)	90	1700

To analyse the product gas, 25 c.c of each sample gas was taken out from the gas bottle and fed to the Orsat apparatus. The percentage of methane gas in the biogas was determined by following the same steps based on the working principle of the Orsat apparatus, as described in Chapter-2. The data obtained from the above analysis have been shown in Table 3.3.

3.2 Results and discussions:

The data obtained (Table-3.1), after conducting some experiments to find BOD, COD, VS and pH of the each of the slurry of the five samples containing cow-dung and the mixture of cow-dung and kitchen-wastes, indicate that all five kitchen-wastes, selected for the biogas production, are biodegradable, because the above values are within the range of bio-degradability of the waste materials as reported by the previous investigators [32] Banana-peels have a higher bio-degradability than other kitchen-wastes.

The data obtained (Table 3.2) for the daily biogas production of each sample containing the slurry of the waste materials, have been plotted to show the variation of the amount of biogas produced by the each sample in 90 days and that of the cow-dung alone. The above variations have been

TABLE - 3.3

Percentage of methane in the biogas generated by each of the samples of the kitchen-wastes in 12 weeks

Percentage of methane

Period	Cow-dung +water	Cow-dung+ Tea-leaves +water	Cow-dung+ Banana-peels+Water	Cow-dung+ orange-peels +water	Cow-dung+ Potato-peels +water
1st Week					
2nd Week	52.5	52.5	52.6	50.0	52.0
3rd Week	53.1	53.1	54.0	50.0	53.2
4th Week	54.1	54.0	55.0	50.0	54.2
5th Week	55.0	55.0	56.0	50.5	55.4
6th Week	56.1	56.1	57.0	51.0	56.2
7th Week	56.2	56.3	58.0	51.0	56.6
8th Week	56.2	56.3	58.0	-	56.6
9th Week	56.2	56.3	58.0	-	56.6
10th Week	56.2	56.3	58.0	-	56.6
11th Week	56.1	56.2	57.9	-	56.5
12th Week					

shown in Fig. 3.1. It can be seen that for a retention time of 90 days, sample-3 containg the slurry of the mixture of cow-dung and banana peels, can produce more biogas than other samples, where as sample-4, containing the slurry of the mixture of cow-dung and orange peels, can produce the least amount of biogas. It may be due to the fact that banana peels help in growing the population of methanogenic bacteria than other kitchen-wastes, whereas, orange-peels act as the toxic material for the above bacteria, causing the adverse effects on the growth of the population of the above bacteria. The degree of biogas generation capacity of the different kitchen-wastes is found to be in the ascending order of

orange-peels < tea-leaves < potato-peels < banana-peels

The data obtained for the weekly analysis of biogas produced by the each sample using the Orsat apparatus, have been plotted to show the variation of the methane content in the biogas in 12 weeks. The above variations have been shown in Fig. 3.2. It can be observed that the percentage of methane increases as the retention time increases. It may be due to the reason that the activity of the methane producing bacteria increases as the retention time increases.

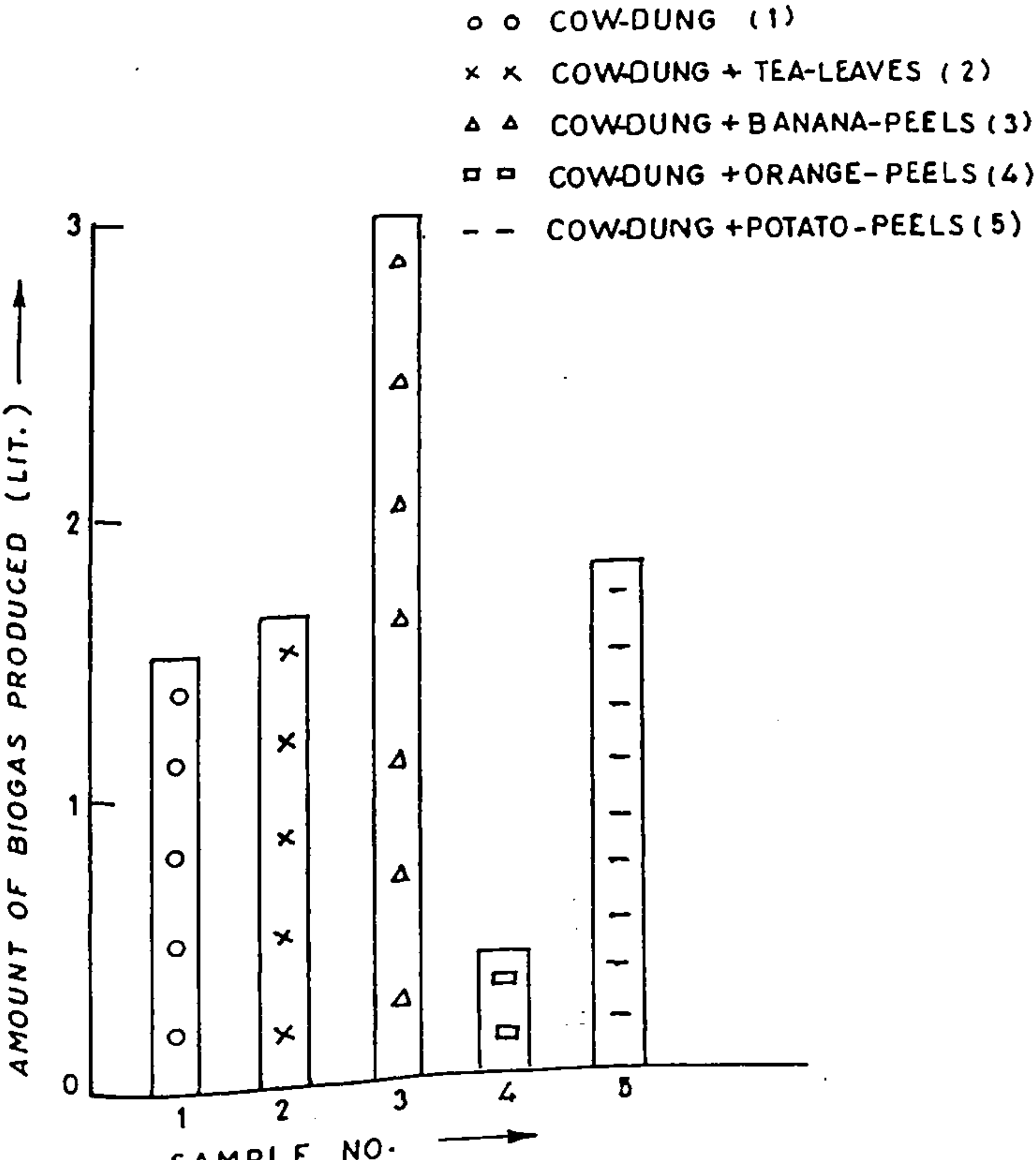


Fig. 3.1 : BIOGAS GENERATION CAPACITY OF THE EACH OF THE SAMPLES OF KITCHEN WASTES.

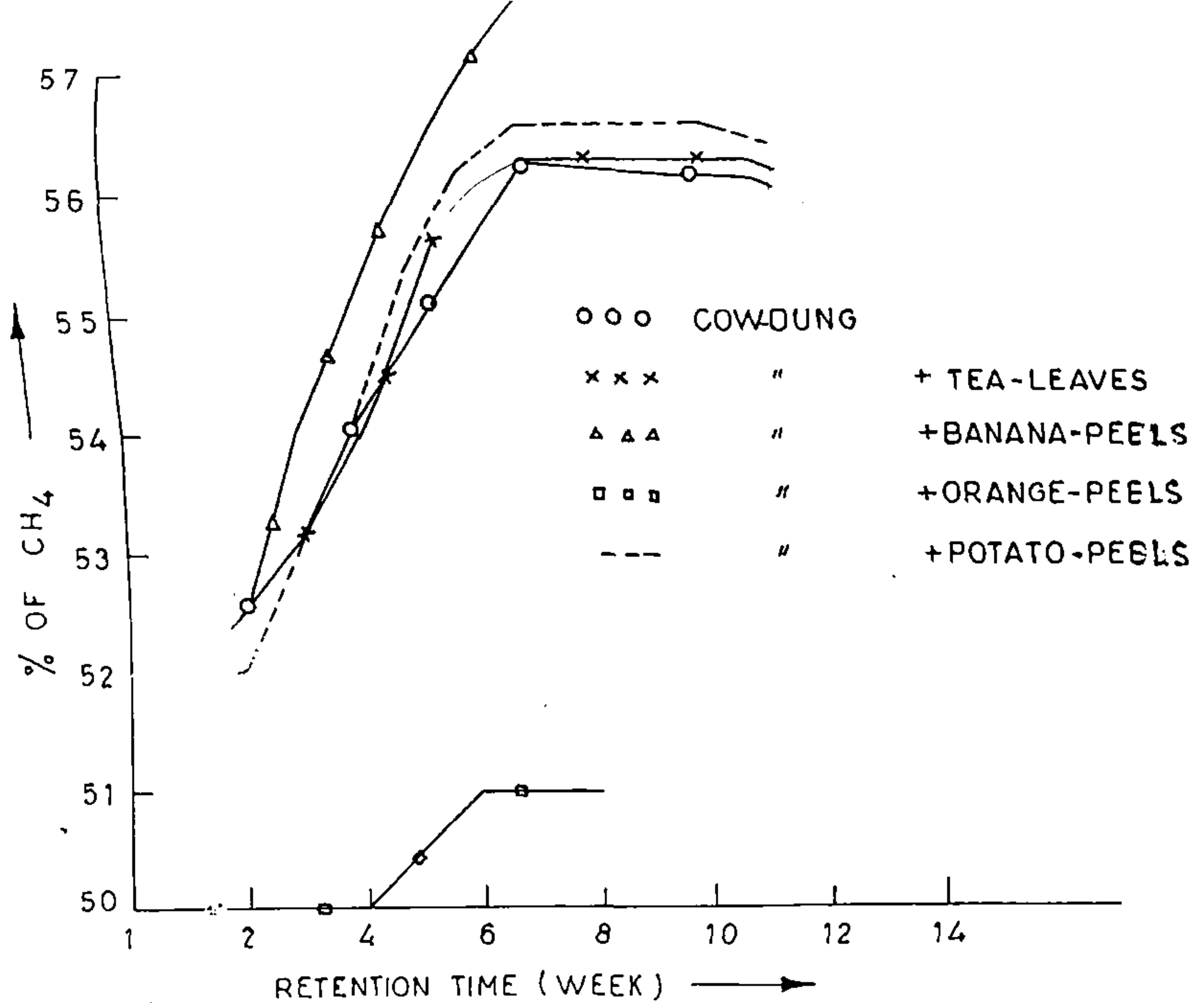


FIG. 3.2 : VARIATION OF % OF CH_4 WITH RETENTION TIME

The results of the experiments described above may be utilized to study the bio-degradability of other wastes and investigate the biogas generation capacity of the other kitchen-wastes not selected for the above experiments.

CHAPTER - 4

A COMPARATIVE STUDY OF BIOGAS PRODUCTION FROM THE MIXTURES OF COW DUNG AND WASTE FLOWERS

CHAPTER - 4

A comparative study of biogas production from the mixtures of cow-dung and Waste flowers

Flowers are generally used for worship, decoration and extraction of perfumes. These flowers become useless when they are thrown away after use. But valuable energy can be obtained from these waste flowers when these are utilized in anaerobic digesters. These waste materials can be mixed with cow-dung and can be used as raw materials for biogas production.

In this Chapter, an attempt has been made to present the results of some experiments conducted for the slurry of the cow-dung alone and the mixtures of cow-dung and waste flowers as raw materials for the laboratory scale anaerobic digesters used for biogas production.

The following waste flowers were selected for the above experiments:

i) Marigold

ii) Sunflower

iii) Oleander

iv) Balsam

The above flowers were collected from the sorrounding areas

4.1 Experiments:

To conduct some experiments for the production of biogas from the waste flowers, one sample containing the slurry of cow-dung and five samples containing the slurry of the mixture of cow-dung and waste flowers were used.

The above five samples were as follows:

Sample-1: The mixture of cow-dung and water (1:1)

Sample-2: The mixture of cow-dung, Marigold and water (1:1:2)

Sample-3: The mixture of cow-dung, Sunflower and water (1:1:2)

Sample-4: The mixture of cow-dung, Oleander and water (1:1:2)

Sample-5: The mixture of cow-dung, Balsam and water (1:1:2)

Preparation of the samples:

To conduct some tests, the slurry of each of these five samples was prepared. The general procedure of preparing the above samples was as follows:

To prepare Sample-1, 200 g of cow-dung was mixed with 200 g of water in a flask and shaken well. To prepare other five samples, at first, each waste flower was ground to make a paste and it was then mixed in equal amount with 100g of cow-dung. 200 g of water was added to make a slurry.

The following tests were conducted for each of the above five samples:

i) Determination of COD, BOD, VS and pH of the samples.

ii) Determination of total amount of biogas produced by the samples in the anaerobic digesters.

iii)Determination of methane content in the biogas produced by the samples, using the Orsat apparatus.

4.1.1 Determination of COD, BOD, VS and pH of the samples:

To find out the bio-degradability of these samples and thereby predict the biogas generation capacity, COD, BOD, VS and pH were determined for each of the samples. A part (50 c.c) of the prepared slurry of each sample was taken for the above purpose. Each sample was tested to determine the above parameters using standard method as described in Chapter-II. The test results have been shown in TABLE-4.1.

4.1.2 Determination of total amount of biogas produced by the samples in the anaerobic digesters:

To study the biogas generation capacity of each sample, consisting of 300 c.c. slurry, each of the five samples, was placed into six 500 c.c bottles which were used as the biogas generators. All the five digesters were kept inside a thermostat for a retention period of 90 days. The

TABLE 4.1

COD, BOD, VS and pH of each of the samples of the waste flowers

Sample	COD (mg/l)	BOD (mg/l)	VS (mg/l)	pH
1. Cow-dung +water	9320	4293	4352	6.4
2. Cow-dung +Marigold+ water	9800	5721	5155	6.4
3. Cow-dung+ Sunflower +water	9523	2425	2430	6.4
4. Cow-dung+ Oleander +water	10000	5896	6661	6.4
5. Cow-dung+ Balsam +water	9350	3000	3016	6.4

temperature of the thermostat was kept constant at 37 ± 1oC. Each digester was agitated 5 to 6 times daily with the help of the magnetic stirrer to keep the mixture of the slurry of a uniform consistency and to distribute the population of the bacteria in all parts of the slurry. The gas produced by each digester was collected by the displacement of acidified water in a graduated measuring bottle. The amount of biogas generated by each sample was measured daily and thus the total amount of biogas produced by the each sample in 90 days was determined. The results have been shown in Table-4.2.

4.1.3 Determination of methane content in the biogas produced by the samples using the Orsat apparatus:

The biogas generated by the each sample was analyzed once in a week to determine the methane content in it and its quality. The analysis was done using the Orsat apparatus. Thus the variation of the methane content in the biogas generated in 90 days was found out.

To analyse the product gas, 25 c.c of each sample was taken out from the gas bottle and fed to the Orsat apparatus. The percentage of methane gas in the biogas was determined by following the procedures described in Chapter-2. The data obtained for the above analysis have been shown in Table-4.3.

TABLE - 4.2

Total amount of biogas generated by each of the samples of the waste-flowers

Total volume of the slurry in each digester = 300 c.c

Composition of the sample	Retention time (days)	Total amount of biogas generated(c.c)
Sample-1: Cow-dung and water (1:1)	90	2500
Sample-2: Cow-dung, Marigold and water (1:1:2)	90	2000
Sample-3: Cow-dung,Sunflower and water (1:1:2)	90	1000
Sample-4: Cow-dung, Oleander and water (1:1:2)	90	2600
Sample-5: Cow-dung, Balsam and water (1:1:2)	90	1900

TABLE - 4.3

Percentage of methane in the biogas generated by each sample of the waste flowers

Percentage of methane

Period	Cow-dung +water	Cow-dung+ Marigold +water	Cow-dung+ Sunflower +water	Cow-dung+ Oleander +water	Cow-dung+ Balsamn +water
1st Week					
2nd Week	53.0	53.0	52.0	53.0	52.0
3rd Week	53.2	53.2	52.3	53.4	52.4
4th Week	53.7	53.9	53.6	54.0	53.1
5th Week	54.9	55.9	54.7	55.0	55.0
6th Week	56.5	56.2	56.0	56.1	56.2
7th Week	56.6	56.7	56.1	56.7	56.6
8th Week	56.7	56.7	56.0	56.8	56.5
9th Week	56.7	56.6	-	56.8	-
10th Week	56.5	56.5	-	56.7	-
11th Week	56.5	56.5	-	56.7	-
12th Week					

4.2 Results and discussions :

The data obtained (Table-4.1) for the tests of BOD, COD, VS and pH of the each of the five samples containing cow-dung alone and the mixtures of cow-dung and waste flowers, indicate that Oleander flower is most bio-degradable and Sun flower is least degradable among the waste flowers used for biogas production. It may be due to the fact that the slurry of the mixture of cow-dung and Oleander has higher COD and BOD than that of the cow-dung and the slurry containing the mixture of cow-dung and Sunflower has less COD, and BOD than that of the slurry of cow-dung.

The data obtained, regarding the daily gas production of the six samples containing the waste materials have been plotted to show the variations of the amount of biogas produced by each sample. Table- 4.2 gives these details. The variations in the bio gas production have been shown in Fig. 4.1.

It can be observed that among the five samples, sample-4 containing the slurry of the mixture of cow-dung and Oleander can produce maximum biogas whereas, sample-3 containing the slurry of the mixture of cow-dung and Sun-flower can produce less amount of biogas than other samples. It may be due to

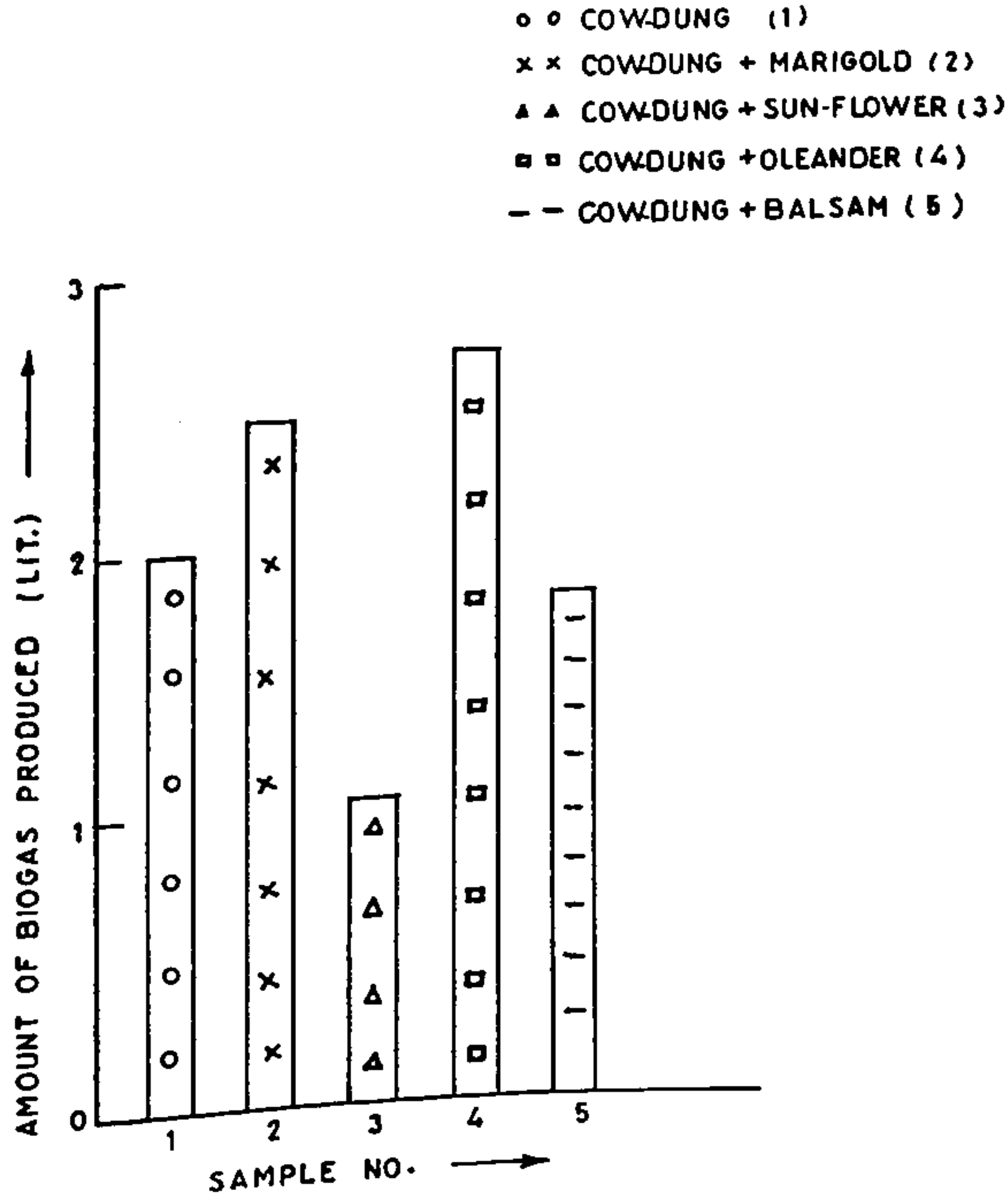


Fig. 4.1 : BIOGAS GENERATION CAPACITY OF THE EACH OF THE SAMPLES OF THE WASTE FLOWERS.

the fact that the Oleander is the most bio-degradable among these and hence it can help in the growth of the population of methanogenic bacteria which is responsible for the generation of the biogas, where as, the Sun-flower has the adverse effects on the growth of the population of the above type of bacteria due to the toxicity of the slurry.

The data obtained (Table-4.3), for the weekly analysis of biogas produced by the five samples in 12 weeks, using the Orsat apparatus, have been plotted to show the variation of the methane content and hence the quality of the biogas. The above variations have been shown in Fig. 4.2. It can be seen from the above variations, that the methane content in the biogas increases as the retention time increases for the each sample. It may be due to the fact that in the beginning, each sample produces more CO_2 but less CH_4 and as the retention time increases percentage of CH_4 also increases.

The results of the above experiments may be utilized to study the bio-degradability of other waste flowers. Further, these might lead to a better understanding of the biogas generation capacity and the quality of the biogas of waste flowers in general.

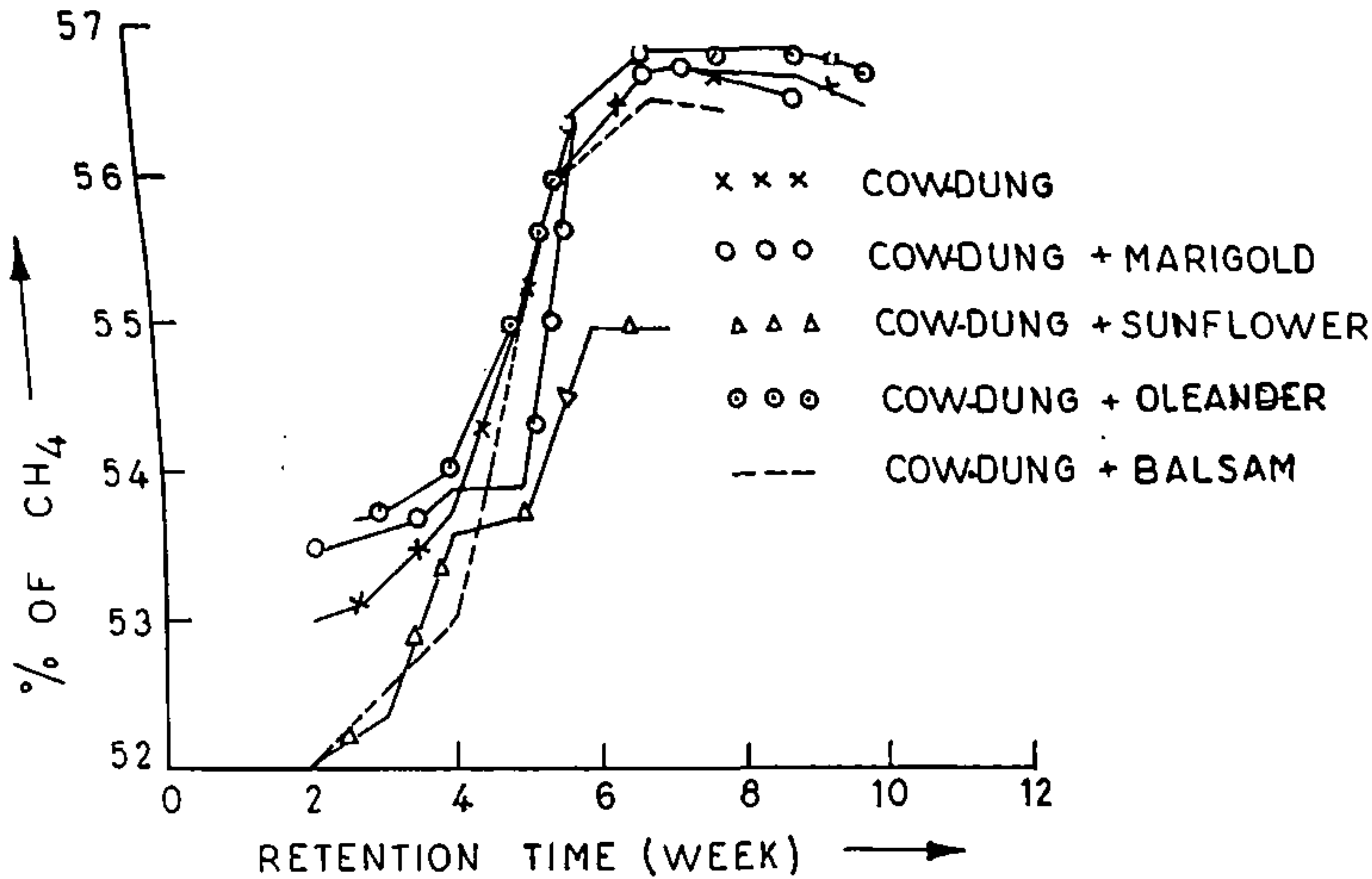


Fig. 4.2: VARIATION OF % CH_4 IN BIOGAS WITH RENTENTION TIME

CHAPTER - 5

A COMPARATIVE STUDY OF BIOGAS PRODUCTION FROM THE MIXTURES OF COW-DUNG AND WASTE LEAVES AND VEGETABLES

CHAPTER - 5

A comparative study of biogas production from the mixtures of cow-dung and waste leaves and vegetables

A huge amount of waste vegetables and leaves, which are collected from the agricultural lands, gardens and vegetable markets, are not used by the human beings or nor fed to the cattles are dumped on the earth. These waste materials cause environmental pollution due to their foul smell etc, when they decompse on the earth in the presence of air, heat, etc. But these waste materials can be utilized in the anaerobic digester to produce a valuable biogas that can be used for cooking, lighting, etc.

In this Chapter, an attempt has been made to present the results of some experiments done on the laboratory scale anaerobic digesters to make a comparative study of biogas produced by the mixtures of cow-dung and some waste leaves cow-dung and the mixtures of cow-dung and waste vegetables.

The waste vegetables and leaves which were selected for the above experimens are mentioned below :

1) Rotten potato

2) Cabbage

3) Potato-leaves

4) Raddish-leaves

5.1 Experiments:

To conduct some experiments for the production of biogas from the waste vegetables and leaves, one sample containing the slurry of cow-dug and four samples containing the slurry of the mixtures of cow-dung and different waste vegtable/leaves used. The above five sample were:-

Sample-1: The mixture of cow-dung and water (1:1)

Sample-2: The mixture of cow-dung, rotten potato and water (1:1:2).

Sample-3: The mixture of cow-dung, cabbage and water (1:1:2)

Sample-4: The mixture of cow-dung, potato-leaves and water (1:1:2)

Sample-5: The mixture of cow-dung, raddish-leaves and water (1:1:2)

Preparation of the samples:

Before conducting some tests, it is required to prepare the sample properly. The general procedure of preparing each of the above samples was as follows:

To prepare Sample-1, 200 g of cow-dung was mixed with 200 g of water in a flask and shaken well. To prepare other four samples at first waste vegetables and leaves were ground to make a paste and then it was mixed with equal amounts of 100 g of cow-dung. 200 g of water was added to each of the mixtures of cow-dung and waste vegetables or waste leaves to make a slurry.

The following tests were conducted for each of the above samples:

i) Determination of COD, BOD, VS and pH of the samples.

ii) Determination of total amount of biogas generated by the samples in the anaerobic digesters.

iii) Determination of methane content in the biogas produced by the samples using the Orsat apparatus.

5.1.1 Determination of COD,BOD, VS and pH of the samples:

In order to find out the bio-degradability and to predict the biogas generation capacity of each sample, its COD, BOD, VS and pH were determined. A part of the prepared sample was used for the above purpose. Each sample was tested to determine the above parameters using standard methods described in Chapter-2. The test results have been shown in Table-5.1.

5.1.2 Determination of the total amount of biogas generated by the samples in the anaerobic digesters:

To study the biogas generation capacity of each sample, 300 c.c slurry of each of the five samples, was placed separately into five 500 c.c capacity bottles which were used as the biogas generators. All the five digesters containing the slurry of cow-dung and mixtures of the cow-dung and waste vegetables or leaves, were kept inside the thermostat for 90 days. The termperature of the thermostat was kept constant at a temperature of $37 \pm 1^{o}C$. Each digester was

TABLE 5.1

COD, BOD, VS, and pH of each of the samples of the waste leaves and vegetables

Sample	COD (mg/l)	BOD (mg/l)	VS (mg/l)	pH
1. Cow-dung +water	8200	5084	6062	6.3
2. Cow-dung +rotten potato +water	8975	5860	8855	6.3
3. Cow-dung+ cabbage+water	7520	2346	2347	6.3
4. Cow-dung+ potato-leaves +water	8495	5095	6089	6.3
5. Cow-dung+ raddish-leaves +water	8300	2236	2237	6.3

agitated 5 to 6 times everyday, with the help of magnetic stirrer to keep the slurry of the mixture of a uniform consistency. The biogas produced by each sample was collected by the displacement of acidified water in a graduated measuring bottle. The amount of biogas generated by each sample was measured daily and thus the total amount of biogas produced by each sample in 90 days was determined. The test results have been shown in Table 5.2.

5.1.3 Determination of methane content, in the biogas produced by the samples, using the Orsat apparatus:

The biogas produced by each sample was analysed once in a week to determine the methane conent in it. The percentage of methane in the biogas, in fact, indicates the quality of biogas. High percentage of methane indicates that the biogas has high fuel value i.e., it has high calorific value. The analysis was done using the Orsat appartus. Thus, the variation of the methane content in the biogas generated in 90 days was determined.

TABLE - 5.2

Total amount of biogas generated by each sample of the waste leaves and vegetables

Total volume of the slurry in each digester = 300 c.c

Composition of the sample	Retention time (days)	Total amount of biogas generated(c.c)
Sample-1: Cow-dung and water (1:1)	90	2100
Sample-2: Cow-dung, rotton potato and water (1:1:2)	90	2450
Sample-3: Cow-dung, cabbage and water (1:1:2)	90	1000
Sample-4: Cow-dung, potato-leaves and water (1:1:2)	90	2200
Sample-5: Cow-dung, raddish-leaves and water (1:1:2)	90	500

To analyse the product gas, 25 c.c. of each sample gas was taken out from the gas bottle and fed to the Orsat apparatus. The percentage of the methane gas in the biogas was found out by following the procedures as described in Chapter-2. The data obtained for the above analysis have been shown in Table 5.3.

5.2 Results and discussions:

The data obtained (Table-5.1) after conducting some tests to find out the BOD, COD, VS and pH of each of the slurry of the five samples containing cow-dung, and the mixture of cow-dung and waste leaves/vegetables, indicate that the rotten-potato is the most bio-degradable waste product and the raddish-leaves is the least bio-degradable.

The data obtained (Table-5.2) for daily gas production of each sample containing the slurry of waste materials, have been plotted to show the variations of the amount of biogas produced by the mixtures of cow-dung and waste vegetables/leaves and also the variation of the biogas produced by cow-dung alone. The above variations have been in shown

Table 5.3

Percentage of methane in the biogas generated by each samples of the waste leaves and vegetables

Percentage of methane

Period	Cow-dung +water	Cow-dung+ potato +water	Cow-dung+ cabbage +water	Cow-dung+ potato-leaves +water	Cow-dung+ radish-leaves +water
1st Week					
2nd Week	53.0	53.6	53.1	53.4	53.0
3rd Week	53.2	53.8	53.2	53.6	53.1
4th Week	53.9	54.0	53.7	55.7	53.7
5th Week	55.0	56.2	55.0	56.0	54.0
6th Week	56.4	57.0	55.0	56.8	53.6
7th Week	56.6	57.5	54.9	56.9	-
8th Week	56.7	57.5	-	56.8	-
9th Week	56.6	57.4	-	56.8	-
10th Week	56.5	57.4	-	56.8	-
12th Week					

in the Fig. 5.1. It can be seen that out of 5 samples, sample-2 containing the slurry of the mixture of cow-dung and rotten potato can produce maximum amount of biogas, whereas, sample-5 can produce the least amount of biogas. It may be due to the fact that rotten potato can help more in the growth of the population of methanogenic bacteria than other waste vegetables and leaves and also, the mixture of cow-dung and rotten-potato has higher BOD than cow-dung and other waste vegetables/leaves.

The data obtained (Table-5.3) for the weekly analysis of biogas produced by the each sample using the Orsat apparatus, have been plotted to show the variation of the methane content in the biogas in 12 weeks. The above variations have been shown in Fig. 5.2. It can be observed that the percentage of methane increases as the retention time increases. It may be due to the fact that in the beginning, each sample produces more CO_2 and CH_4 and as the retention time increases the percentage of CH_4 also increases.

From the results of the experiments, it can be concluded that the bio-degradability of the waste leaves and vegetables may could be a good parameter to determine the biogas generation capacity and the quality of the biogas from any other waste vegetables and leaves.

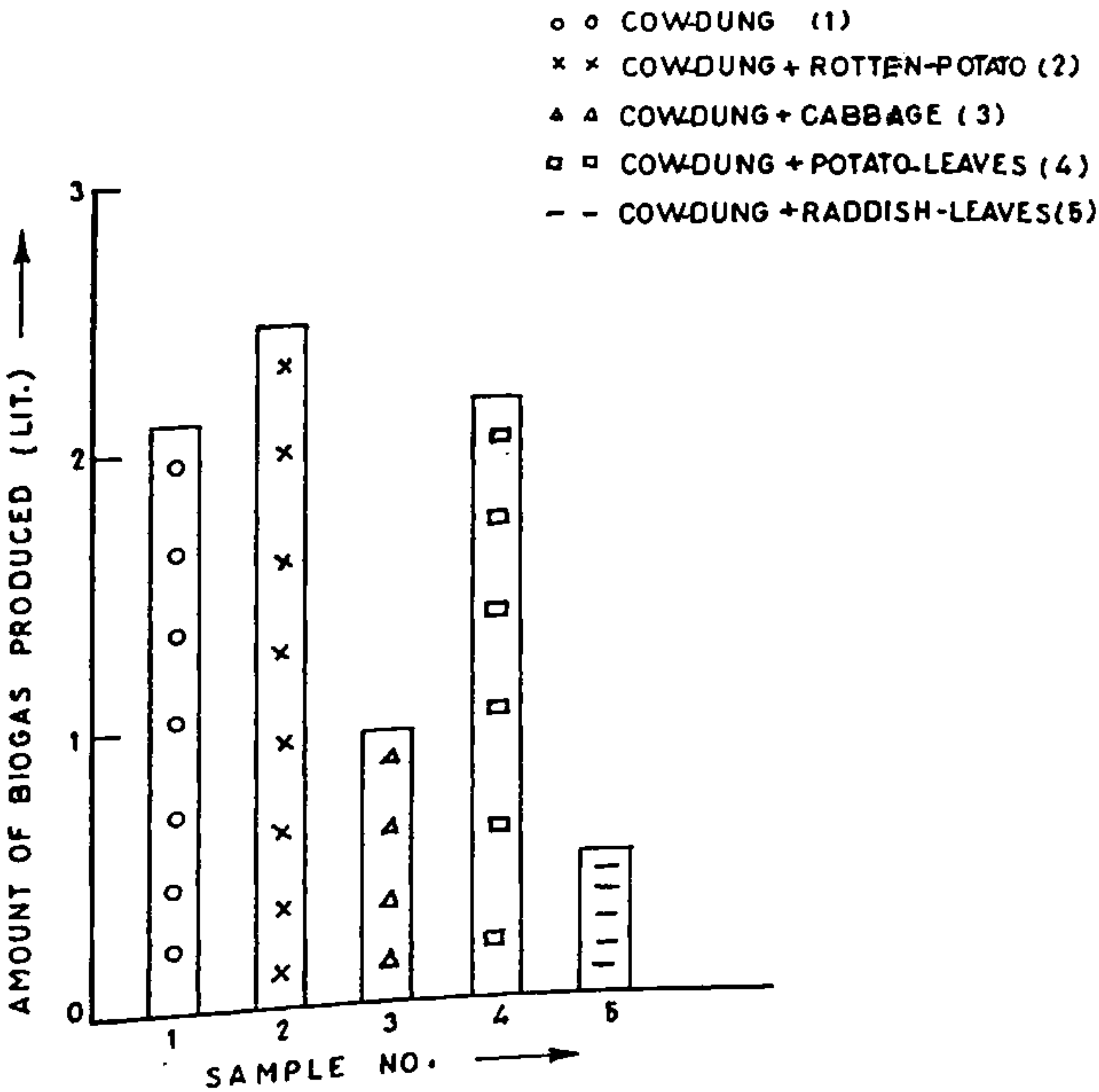


Fig. 5.1: BIOGAS GENERATION CAPACITY OF THE EACH OF THE SAMPLES OF WASTE LEAVES AND VEGETABLES.

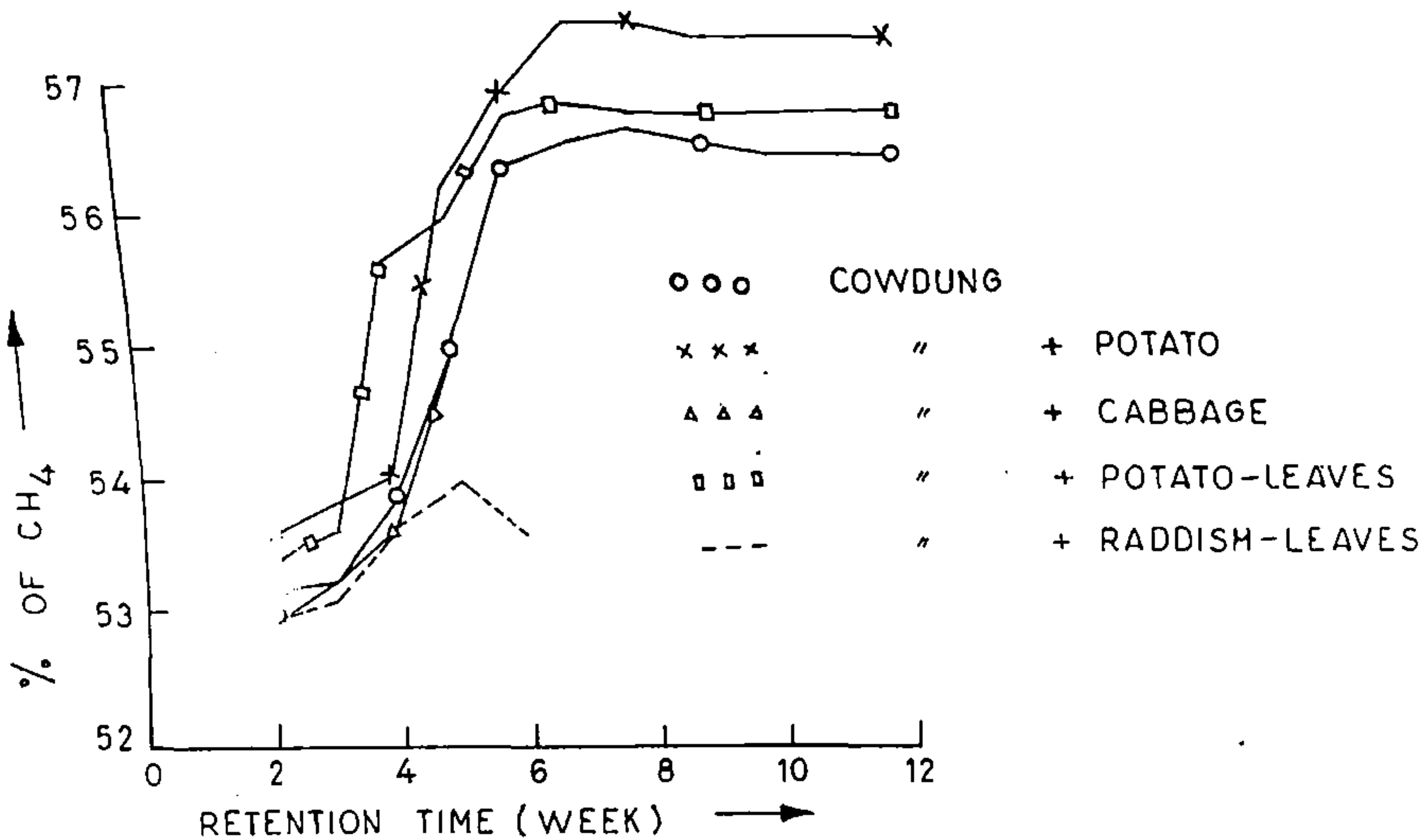


FIG. 5.2 : VARIATION OF % CH_4 IN THE BIOGAS WITH THE RETENTION TIME

CHAPTER - 6

THE EFFECTS OF THE VARIOUS METALLIC CATALYSTS ON THE BIOGAS PRODUCTION

CHAPTER - 6

The effects of various metallic catalysts on the biogas production

A number of experiments have been carried out in various R & D Centres to study the effects of some parameters [33,34] to improve the biogas yield. To increase the total amount of biogas to be produced by an anaerobic digester, it is required to stabilize the digester by controlling COD, BOD, VS and pH, etc. of the slurry. It is found that most of the enzymatic reactions are accelerated by the presence of Mg^{2+}, Cu^{2+}, Cd^{2+}, ions, etc. [30] because their surfaces activate the growth of bacteria. In acid medium metals might generate nascent hydrogen which can reduce CO_2 to CH_4. Waste materials produce biogas due to the presence of methanogenic bacteria. Metals are toxic at higher concentrations for a bio-methanation process. The population of the above type of bacteria can be increased by providing the metallic surface in the waste materials.

In this Chapter, an attempt has been made to study the effects of certain metallic catalysts to improve the yield of the total amount of biogas to be generated from cow-dung by conducting some experiments on the digesters.

The following metallic catalysts were selected for the above experiments:

i) Mg ii) Al iii) Zn iv) Ni v) Fe

The data obtained from the above experiments have been shown in a tabular form, graphically plotted and the results, thus obtained have been discussed.

6.1 Experiments to study the effects of the metallic catalysts on the biogas production from cow-dung:

To conduct experiments thirty one anaerobic digesters, each having a capacity of 500 c.c, have been used. They were kept inside the thermostat to maintain the temperature of the digester at $37^{o}C \pm 1^{o}C$. The retention time was 90 days for the each sample.

The following experiments have been conducted on the digesters:

i) To find out the total amount of biogas generated by the digesters containing the slurry of cow-dung in 90 days, with and without adding small traces of different amounts (mg) of 'Mg' catalyst for the purpose of finding out also the optimum value of the amount of Mg catalyst for which maximum amount of biogas can be generated.

ii) To find out the total amount of biogas generated by the digesters, with and without adding small traces of different amounts of 'Al' catalyst to find its optimum value for which maximum amount of biogas can be generated.

iii) To find out the total amount of biogas generated by the digesters, with and without adding the small traces of different amounts of 'Zn' catalyst and record its optimum value for which maximum amount of biogas can be generated.

iv) To find out the total amount of biogas generated by the digesters, with and without adding the different amounts (mg) of 'Ni' catalyst and to find its optimum value for which maximum amount of biogas can be generated.

v) To find out the total amount of biogas generated by the digesters, with and without adding small traces of different amounts of 'Fe' catalyst and find its optimum value for which maximum value of the biogas can be generated.

The data obtained from the above experiments have been shown in the Tables 6.1, 6.2, 6.3, 6.4 and 6.5.

6.2 Results and Discussions:

The data obtained for the experiments as described in the previous section can be used to study the performances of the digesters used for biogas production. Figure 6.1 shows the total amount of biogas produced by each digester with different amounts of five catalysts for a retention period of 90 days. It can be seen that without adding any catalyst the digester containing cow-dung can produce 1.5 litres of biogas but due to the addtion of different amounts of catalyst to the cow-dung, other digesters can produce biogas either above or below 1.5 liters of biogas. It can also be seen that except Fe, other metals can enhance the biogas prodction from the cowdung with the defined amounts of them. It maybe due to the fact that the Fe has a toxic effect on the growth of the population of methanogenic bacteria which is responsible for the generation of biogas where as other metals can provide the surfaces which activate the growth of the above bacteria. The degree of

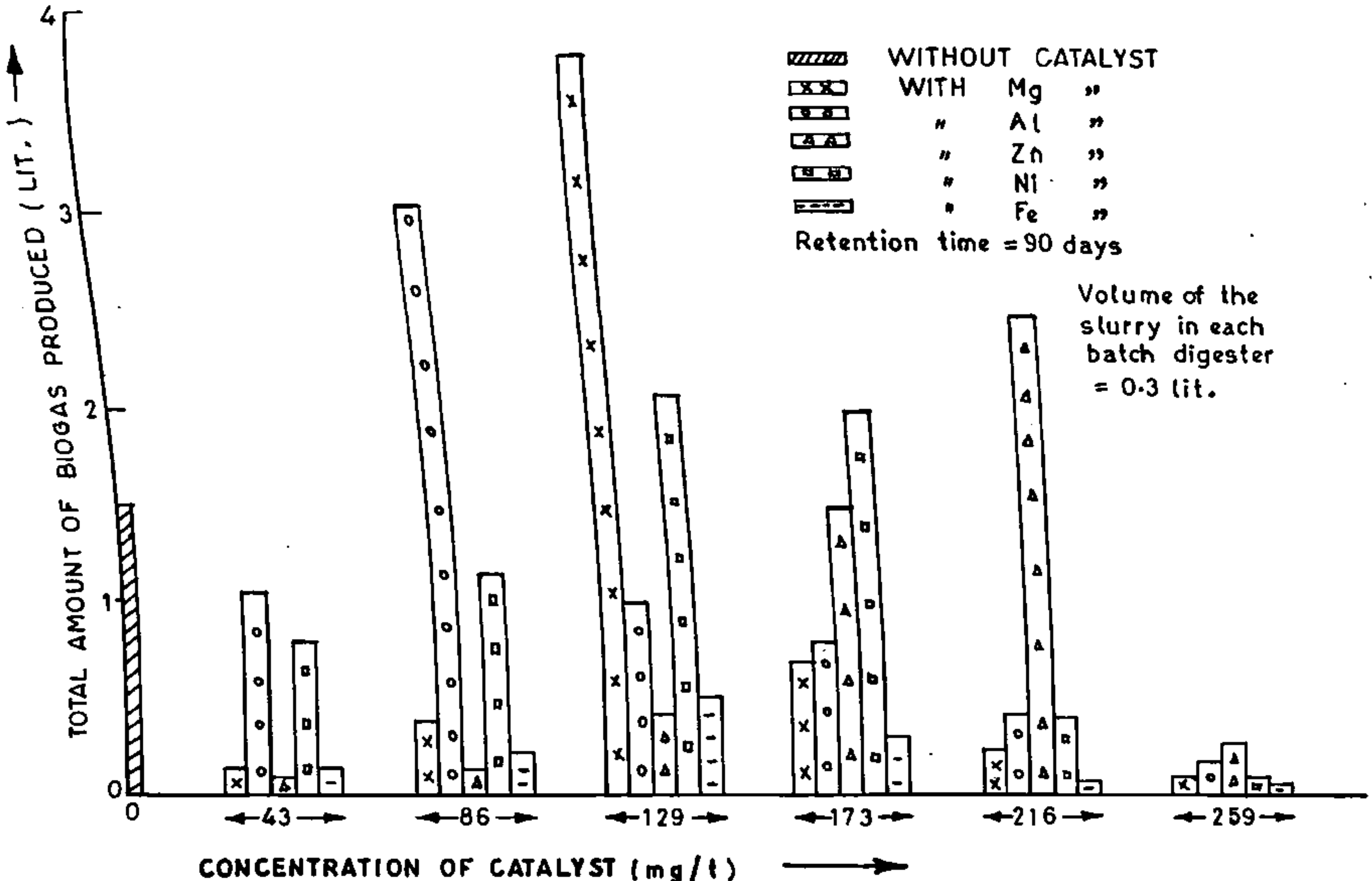


FIG. 6.1: TOTAL AMOUNT BIOGAS PRODUCED BY THE SLURRY OF THE COWDUNG WITH DIFFERENT CONCENTRATIONS OF CATALYSTS

Table 6.1

Total amount of biogas produced by cow-dung with Mg catalysts

Nature of Slurry: Cowdung and Water(1:1)

Volume of the Slurry = 300 c c

Temperature of the slurry = 37 ± 1°C

Retention time = 90 days

Concentration of the catalyst (mg/l)	Total amount of biogas produced (c.c.)
0	1500
43	100
86	400
129	3850
173	600
216	200
259	60

Table 6.2

Total amount of biogas produced by cow-dung with Al catalyst

Nature of Slurry: Cow-dung and Water(1:1)

Volume of the Slurry = 300 c c

Temperature of the slurry = 37 ± 1 °C

Retention time = 90 days

Concentration of the catalyst (mg/l)	Total amount of biogas produced (c.c.)
0	1500
43	1050
86	3000
129	1000
173	800
216	400
259	150

Table 6.3

Total amount of biogas produced by cow-dung with Zn catalyst

Nature of Slurry: Cowdung and Water(1:1)

Volume of the slurry = 300 c c

Temperature of the slurry = 37 ± 1 $^{\circ}$C

Retention time = 90 days

Concentration of the catalyst (mg/l)	Total amount of biogas produced (c.c.)
0	1500
43	90
86	125
129	400
173	1500
216	3500
259	350

Table 6.4

Total amount of biogas produced by cow-dung with Ni catalyst

Nature of Slurry: Cowdung and Water(1:1)

Volume of the Slurry = 300 c c

Temperature of the slurry = 37 ± 1°C

Retention time = 90 days

Concentration of the catalyst (mg/l)	Total amount of biogas produced (c.c.)
0	1500
43	900
86	1200
129	2150
173	2000
216	400
259	75

Table 6.5

Total amount of biogas produced by cow-dung with Fe catalyst

Nature of Slurry: Cowdung and Water(1:1)

Volume of the Slurry = 300 c c

Temperature of the slurry = 37 ± 1° C

Retention time = 90 days

Concentration of the catalyst (mg/l)	Total amount of biogas produced (c.c.)
0	1500
43	70
86	150
129	500
173	400
216	10
259	10

activities is found to be in ascending order of

$$Fe < Ni < Zn < Al < Mg$$

Figure 6.2 shows the maximum biogas generation capacities of the digesters with the optimum values of the different catalysts. It also shows the maximum period for which each digester can produce biogas with the optimum values of the catalysts. Following observations were made for the digesters:

i) The digester containing only 300 c.c. cow-dung can produce the maximum amount of 1.5 lit. of biogas in 90 days.

ii) The digester containing 300 c.c. slurry of cow-dung with an optimum value (129 mg/l) of Mg catalysts can produce the maximum amount (3.85 lit.) of biogas in 90 days.

iii) The digester containing 300 c.c. slurry of cow-dung with an optimum value (86 mg/l) of Al catalyst can produce maximum amount (3 lit) of biogas for a period of 75 days. It stops producing biogas after this period. In the above period, it can generate biogas at a fast rate initially but this rate slows down by end of this period. So a fresh slurry of cow- dung is required to be added into the digester after 75 days.

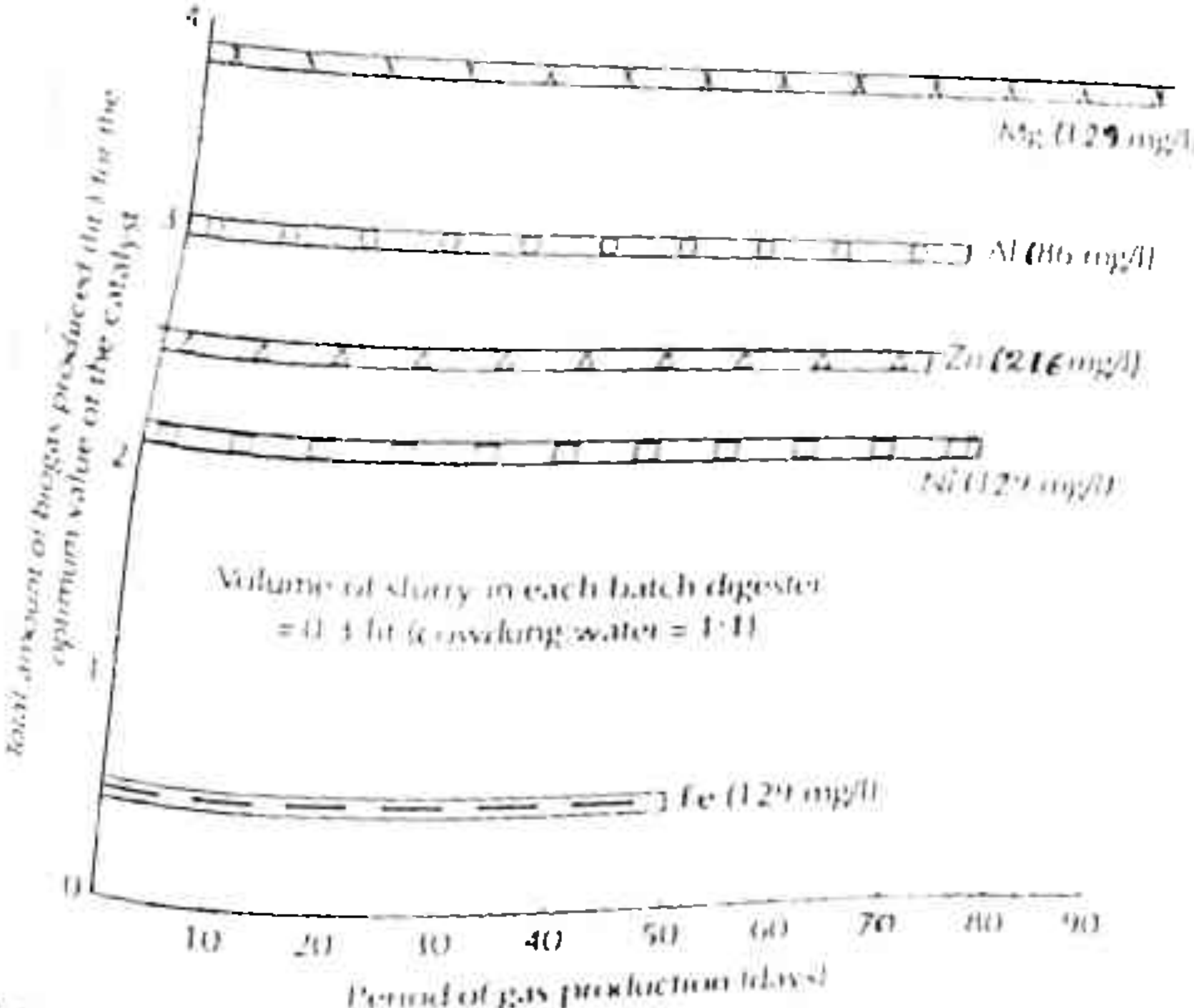


Fig. 6.2: :Biogas generation capacity of the cowdung slurry with optimum values of the catalysts

iv) The digester containing 300 c.c. of slurry of cow-dung with an optimum value of (216 mg/l) Zn catalyst can produce the maximum amount (2.5 lit.) of biogas for a period of 70 days. After 70 days it stops producing biogas. So a fresh slurry of cow-dung is required to be put into the digester.

v) The digester containing 500 c.c. slurry of cow-dung with an optimum value (129 mg/l) of Ni catalyst can produce 2.15 lit. of biogas for a period of 73 days. It stops producing biogas after this period. So a fresh slurry of cow-dung is required to be added into the digester.

vi) The digester containing 300 c.c. slurry of cow-dung with an optimum value (129 mg/l) of Fe catalyst can produce a maximum amount of 500 c.c. biogas in 50 days. The above amount is less than that of the biogas produced by the cow-dung. So Fe catalyst cannot be used for biogas production from the cow-dung.

The above results were obtained at an optimum temperature of 37^{o} C. So, the optimum values of the catalysts for which maximum amounts of biogas generated, will vary at different temperatures.

CHAPTER - 7

CONCLUSIONS

CHAPTER -7

CONCLUSIONS

In this thesis an attempt has been made to present the results of the experiments conducted on the laboratory scale experimental set up of anaerobic digesters taking cow-dung . and other locally available waste biomass, like-kitchen wastes, waste flowers and waste vegetables and leaves as raw materials. An attempt has also been made to study the effects of various metallic catalysts to improve the yield in the biogas production of digesters. The above results have been obtained from the proto-type biogas systems. These results are yet to be tested on the big size biogas systems, like community biogas plants, etc.

In Chapter-1, a rigorous effort has been made to review the work done by the previous workers on biogas generating systems making use of different waste materials. From the literature survey it has been found that there are only a few reports on biogas production from the locally available waste materials. There are a large number locally available waste materials. Some of the waste materials such as different kinds of waste flowers, kitchen wastes, waste leaves and vegetables, for which no reports have been published, have been selected for this study. Also, there is hardly any published or unpublished work on the effects of various metallic catalysts on the yields of biogas production. It was decided to perform some experiments by selecting a number of metallic catalysts. Some case studies have been included in the Chapter-1 of this thesis.

In Chapter-2, the functions of the different components of the laboratory scale experimental set up of anaerobic digester, have been explained with the help of a schematic diagram. Various standard methods of determining COD, BOD, VS and pH of slurry of the waste materials have been described.

In Chapter-3, experimental results of biogas production from the mixture of cow-dung and kitchen wastes have been reported. It has been found that out of various kitchen wastes, banana-peels are the best for higher yields of biogas production.

In Chapter -4, the results of some experiments on biogas production from the mixture of cow-dung and the waste-flowers have been reported. It is seen from the results, that out of various waste-flowers, Oleander is the best material to be used with cow-dung to produce higher amount of biogas.

In Chapter-5, the results of some experiments conducted on biogas production from the mixtures of cow-dung and waste leaves have been reported. It shows that rotten potato and potato-leaves are the most suitable waste vegetables and waste-leaves for biogas production.

In Chapter-6, the results of the experiments on the effects of the various metallic catalysts like Mg, Al, Zn, Ni and Fe on the yield of the biogas have been reported. Based on the results obtained in this study the following conclusion can be drawn : Mg is the best catalyst to enhance the biogas production from cow-dung. Al can be used to produce biogas at a faster rate.

Fe catalyst can not be used to enhance biogas production.

From the results obtained from the tests and experiments discussed in Chapters 3-6, it can be seen that the capacity of biogas generation of different waste materials under various groups is found to be in the ascending order of

Rotten-potato < Banana-peels < Oleander

The above results were obtained at a temperature 37°C, however the result would vary at different temperatures. But these results are very useful to study the bio- degradability of the waste material and hence the biogas generation capacity and quality of the biogas to be produced from other waste materials which were not selected for the study. The effects of metallic catalyst may also be studied on the other waste materials not selected for the above experiments.

The study of biogas generation from different waste materials, is very useful in selecting the biomass to be used for biogas production on a large scale for community bio gas plants. Because all the solid wastes generated daily in ever-increasing quantities from urban, agricultural and industrial sectors cannot produce biogas. Again, some waste materials are inhibitory in by nature and the digesters fail to produce biogas when the slurry

of these waste materials are used. The bio-
degradability of waste materials is judged by
conducting BOD test. From the results of various
experiments, it is established that the BOD value could be a
good parameter to indicate the capacity of biogas generation
of a vaste material. So BOD test is required for an
unknown waste material to be used for biogas production.
For example, in this study it has been seen that among
the various kitchen-wastes orange-peels have a low BOD
value and it also decreases the biogas generation capacity of
the digester when a mixture of cow-dung and this waste
material is used in the digester. So, orange-peels must be
removed from the mixture of the kitchen wastes to produce
biogas.

To enhance the biogas production it is required to
add a small amount of catalyst to accelerate the
process of anaerobic digestion. In this process, the
maximum amount of energy in the form of biogas can be
extracted from the waste materials. But a promoter is
generally required to increase the activity of the
catalyst. So, further studies can be carried out to
use a suitable catalyst and its promoter so that
biogas can be generated from the different bio-

degradable waste materials effectively and efficiently in an anaerobic digesters .

Experiment can be conducted at different temperatures and pretreatment process can be followed in future.

REFERENCES

1. Sheng G.X., 'Biomass Gasifiers: From Waste to Energy Production', Biomass 20, 3-12 (1988).

2. Turick C.E., Peak M.W., Chynoweth D.P. and Jegers D.E., 'Methane Fermentation of Woody Biomass', Biosource Technology, 37, 144-147 (1991).

3. Pimental D. and Vergara W., Aympoaium Papers: Energy from Biomass and Wastes, Washington, D.C., Institute of Gas Technology, pp 87 (1978).

4. Baruah J.N; Raghavan K.V. and Srivastava R.C., 'Kinetics of Biogas Generation from Water Hyacinth', The Chemical Engineering Journal, 40 B21-B24 (1989).

5. Tong X.; Smith L.H. and McCarty P.L., 'Methane Fermentation of Selected Lignocellulose Materials', Biomass, 21, 239-225 (1990).

6. Puhakka J.A., 'Anaerobic Treatment of Kraft Pulp-Mill Waste Activated Sludge" Sludge Dewaterability and Filtrate Quality', Biosource Technology, 39, 69-75 (1992).

7. Modamdar D., Patel A. and Patel V., 'Effects of Various Surfactants on Anaerobic Digestion of Water Hyacinth-Calttle dung', Bisource Technology 37, 157-160 (1991).

8. Singh R.B., 'Biogas plant: Generating Methane from organic Wastes', Ajitmal, Etwash (U.P) India:Gobar Gas Research Station (1971).

9. Chawla O.P., 'Advances in Biogas', Technology: Indian Council of Agricultural Research, New Delhi (1986).

10. Chakraborti R.K. and Guha D., 'Biogas: An Overview, and the role of enzyme extract and anchored enzymes in enhanced and methane-enriched biogas production', Research and Industry, 36, 114-123 (1991).

11. Gobar Gas - Retrospect and prospects-published by Directorate of Gobar Gas Scheme, Khadi and Village Industries Commission, Bombay (1978).

12. 'Biogas production from Mixtures of Cowdung and Saw-dust; A Project Report - United Nations University Training Programme, New Delhi (1989).

13. Molnar L. and Bartha I., 'Solid Waste Methane generation', Journal of Applied Microbiol Biotechnol 4(4), 481-490 (1988).

14. Dwen E.W., Energy from Biomass, Prentice Hall of India, Private Limited, New Delhi (1982).

15. Taiganides B.P., Compost Science, 3, 26 (1963).

16. Bryant M.P., Microbial Energy Conversion, pp 170, Germany (1976)

17. Hawkes D., Horton R. and Stafford D.A., Process Bio-chemistry, 11, 32 (1976).

18. Hobson P.N., Bousfield and Sumners R., Critical Reviews in Environmental Control, pp 131, eleveland (1974).

19. Paynter M.J.B and Hungate J.; J. Bacteriol, 95, 1943 (1968).

20. Khandelwal K.C. and Mahdi S.S., Biogas Technology: A Practical Handbook Tata McGraw-Hill Publishing Company Limited, New Delhi (1986).

21. Clausen, E.e; Sitton, O.C and Gaddy, T.L., Design and Economics of Methane Production from Crop materials, AIChE Symposium, Sr. No. 172, 74, pp 110-116 (1978).

22. Bisaria, VS and Ghosh, T.K - Biodegration of Cellulosic material: Substrate, microorganisms enzymes and products, Enzyme Microb, Techn ol. 3, pp 90-104 (1981).

23. Tars, M.J.; Greenberg, A.E and Hoak R.D., Standard Methods for the examination of Water and Waste Water (13th Edition) American Public Health Association, Washington D.C. (1968).

24. Mathur, R.P., Water and Waste Water Testing, Nemchand & Bros., Roorkee (1985).

25. D.L. Klass, *Symposium paper : Engery from Biomass* and wastes, washigon, D.C., Institute of Gas Technology, pp 1 (1978)

26. C. Chiranjivi, Symposium paper: Engery from Biomass and Wastes, Washigton, D.C., Institute of Gas Technology (1985).

27. Madamwar Datta, Optimization of Biogas production, Ph.D. thesis, BITS, Pilani (1985) .

28. Shinnawi M.M. et.al., Biogas production from crop residues and poutry Wastes, Biomass, Vol. 5, pp 44-48 (1990)

29. Wong M.H. et.al., Biogas Production from pig manure and different agro-industrial waste, Biosource Technology, pp 121-124, Vol. 7 (1991).

30. Sarada R. et.al., Methane production from tomoto- processing waste, biomass, Vol. 6, pp-47 (1993).

31. Vaviline V. A, et.al, Effective biogas production during anaerobic conversion of complex organic matter, Biomass, Vol. 2, pp 48-54 (1994).

32. Mc Carty P.L, Anaerobic waste treatment fundamentals, Public Works, 95 (1964).

33. Lawrence A.W., Mc Carty P.L., The toxicity of heavy mental ions to anaerobic digestion, Journal of Water Pollution Control Federation, 74 : 18-39 (1975).

34. Nyns E.J., Biomethanation process in biotechnology, Bio technology (H.J. Rehm, G.Read(eds.), 8:207-267 (1986).

35. Pandey G.N. and Carney G.C Environmental Engineering p:384-385(1989). Tata Mc Grow Hill Publishing Co. Ltd..

36. Singh Harpal, Singh R. and Pandey K.C., Journal of Solar Energy Society of India, 4(2):59-72(1994).

37. Nagori G.P., Desai H.S. and Rao C.S., SESI Journal 4(1):9-16(1994).

38. Kalia Anjan K., Kanwar Sarbjit, SESI Journal, 5(2):61-68 (1995).

39. Wong M.H., Hobson P.N., Solar Energy 98 (2), PP. 101-107(1993).

40. Dhawale M. R. , Danawade L.N., Biogas Forum : II(50), PP. 7-11(1992).

41. Rande D.R., Nazifan Nagarwala Dudhate J.A., Gadre R.V., Godbole S.H., Indian Journal of Environmental Health, 32(1), PP. 63-63 (1990)

42. Boopathy R., Energy from Bioconversion of Waste Materials, Noyes Data Corporation, USA(1977).

43. Shaha A.K., Combustion Engineering and Fuel Technology, Oxford and IBH Publishing Co. New Delhi, P. 115-119(1982).

44. Hollman J.P., Exprementa1 Method of Engineers, 6th Edition (1995).

45. Rajaskhran <u>et al</u>, Biogas production from the mixtures of cow-dung and euphorbia leaves, SESI Journal, 6(2) pp 6-10 (1993).

46. Rohella <u>et al</u>, Biogas generation from agro-wastes, SESI Journal, 2(1), pp 48-55 (1992).

47. Sharma Archana, Bio-methanation fo some organic wastes, (Ph.D. Thesis), PRL, Jhorhat, Assam (1992).

List of the publications:

1. T. Mandal, N. K. Mandal and V. S. Rao, 'Study of the effects of various metallic catalysts on biogas production', Journal of Solar Energy Society of India, 5(1), PP 1-6(1995).

2. Tanusri Mandal, N. K. Mandal and V. S. Rao, 'Comparative study of biogas production from different waste materials', International Journal of Energy Conversion and Management (in press, 1996).

3. N. K. Mandal and T. Mandal, 'Role of some Non-conventional Energy systems in Environmental Pollution Control', Proc. Ninth National Convention of Environmental Engineers, Jaipur, PP 9-12 (1994).

4. T. Mandal, N. K. Mandal and V. S. Rao, 'Biogas production from different waste flowers', Proc. The Indian Engineering Congress on Technology for Better Tomorrow, PP 75-81(1994).

5. T. Mandal and N. K. Mandal, 'Selection of waste Biomass using COD and BOD methods for higher amount of Biogas production', Proc. The Ninth International Conference on Solid Waste Management', U.S.A., PP 36-41 (1993).

6. T. Mandal and N. K. Mandal, 'Conversion of some waste materials into valuable products', World Congress-III on Engineering and Environment, P. R. China, PP 172-176 (1993).

7. T. Mandal, V. Pirasana and C. Unikrishnan, 'Determination of BOD, COD and VS of some waste materials used for biogas Production', Proc. Seminar on 'Issues in Energy', BITS, Pilani, PP 86-89 (1993).

8. T. Mandal and V. S. Rao, 'Conversion of some pollution making waste materials into valuable products', Proc. UGC Seminar on Environmental Pollution and Waste Treatments, BITS, Pilani, PP 186-19[illegible] (199[illegible]).

9. N. K. Mandal and T. Mandal, 'Role of some Non-conventional Energy Systems in conserving energy in rural areas', Proc. International Symposium in Housing, Energy and Environment, IIT, Delhi, PP 19-25 (1996).

Article No: ECM 576

Date 13-JUN-96

DR NK MANDAL
BIRLA INST OF TECH & SCI
ENGINEERING TECHNOLOGY GROUP
PILANI 333 031 RAJASTHAN
INDIA

ELSEVIER SCIENCE

Elsevier Science Limited

The Boulevard
Langford Lane
Kidlington
Oxford
OX5 1GB
UK

Tel (+44) (0) 1865 843000
Fax (+44) (0) 1865 843010

Dear DR MANDAL

Re: Comparative study of biogas production from different waste materials

I am writing to enlist your help with regard to the above mentioned manuscript which has been received for publication in the journal

ENERGY CONVERSION AND MANAGEMENT

Enclosed please find a copy of the transfer of copyright agreement. It is essential that you sign and return this as quickly as possible so that we can ensure there is no delay in the reproduction of your article.

Thank you in advance for your cooperation.

Yours sincerely

JL BANNISTER
PRODUCTION EDITOR

Imprints:
Elsevier
Pergamon
North Holland
Excerpta Medica

Registered Office
The Boulevard
Langford Lane
Kidlington

COMPARATIVE STUDY OF BIOGAS PRODUCTION FROM THE DIFFERENT WASTE MATERIALS

Tanusri Mandal, N. K. Mandal* and V. S. Rao

Engineering Tecnnology Group
Birla Institute of Technology and Science
Pilani-333031, Rajasthan, India

ABSTRACT: Experimental studies have been carried out to find the biogas generation capacity of the each mixture and its individual component of the various categories of waste materials, like - animal dungs, kitchen wastes, waste flowers, etc. Hence, the best waste material, that can produce maximum amount of biogas from the each category of waste materials, has been found out at a specific temperature of 37°C.

Keywords: Waste materials; Anaerobic digestion; Biodegradable; Retention Period; Biogas.

1. INTRODUCTION

Anaerobic digestion of organic waste to generate biogas has attracted much interest in the recent years [1-3] because of the following facts:

i) It can help in conserving fossil fuels which will not last for many years but will be exhausted in near future.

ii) It can help in controlling environmental pollution which is a great threat to the human life.

iii) It can help in reducing stress on the conventional systems which can not meet the energy demand of the people.

---

*To whom all correspondence should be addressed.

There are various types of waste materials available from different sources. But all waste materials are not biodegradable. Only biodegradable waste materials can produce biogas [4]. Again biogas generation capacity is not same for all the biodegradable waste materials.

In this paper, an attempt has been made to present the results of some experiments conducted on the anaerobic digesters to make comparative study of the biogas generation capacity of the mixture of the each category of the waste materials and its individual components.

2. MATERIALS AND METHODS:

Feedstocks:

To conduct experiments following waste materials, under various groups, were selected.

A. Animal dungs:

i) Cow dung ii) Buffalo dung iii) Camel dung iv) Horse dung.

B. Kitchen Wastes:

i) Tea leaves ii) Banana peels iii) Potato peels iv) Orange peels.

C. Waste Flowers:

i) Sunflower ii) Balsam iii) Marigold iv) Oleander flower.

D. Waste leaves:

i) Cabbage ii) Potato leaves iii) Radish leaves iv) Banana leaves.

Experimental setup:

The major components of the experimental setup (Fig. 1) used for biogas production, comprised digestion units (500 c.c. conical flasks containing the slurry of the different waste materials), a temperature controlled system called thermostat, magnetic stirrers and graduated gas collectors.

Methods:

Twenty samples, as shown in Table I were prepared using the waste materials selected for the experiments. Feed stocks, each in the form of paste, were diluted with distilled water to prepare the above samples. Samples, 300 c.c. each and containing the slurry of waste materials, were dumped into 20 digesters separately, for biogas production.

Table - I

Types of the samples	Sample No.	Composition	Ratio of the components (w/w)
A. Animal dung	1.	Mixture of cowdung, buffalo dung, camel dung, horse dung and water	1:1:1:1:4
	2.	Mixture of cowdung and water	1:1
	3.	Mixture of buffalo dung and water	1:1
	4.	Mixture of camel dung and water	1:1
	5.	Mixture of horse dung and water	1:1

Types of the samples	Sample No.	Composition	Ratio of the components (w/w)
B. Kitchen wastes	6.	Mixture of tea leaves, banana peels, potato peels, orange peels, cowdung and water	1:1:1:1:1:5
	7.	Mixture of tea leaves, cowdung and water	1:1:2
	8.	Mixture of banana peels, cowdung and water	1:1:2
	9.	Mixture of potato peels, cowdung and water	1:1:2
	10.	Mixture of orange peels, cowdung and water	1:1:2
C. Waste flowers	11.	Mixture of sunflower, modar flower, marigold, season flower, cowdung and water	1:1:1:1:1:5
	12.	Mixture of sunflower, cowdung and water	1:1:2
	13.	Mixture of balsam, cowdung and water	1:1:2
	14.	Mixture of marigold, cowdung and water	1:1:2
	15.	Mixture of oleander flower, cowdung and water	1:1:2
D. Waste leaves	16.	Mixture of cabbage, potato leaves, radish leaves, banana leaves, cowdung and water	1:1:1:1:1:5
	17.	Mixture of cabbage, cowdung and water	1:1:2
	18.	Mixture of potato leaves, cowdung and water	1:1:2
	19.	Mixture of radish leaves, cowdung and water	1:1:2
	20.	Mixture of banana leaves, cow dung and water	1:1:2

All the digesters, containing the slurry of the different waste materials, were placed inside the thermostat and allowed to ferment in batch mode for 90 days. The temperature of the thermostat was maintained at 37 ± 1°C. Mixing of the slurry of the each digester was accomplished by magnetic stirrer as well as manually shaking the flask twice a day about 2 to 3 minutes. The gas produced from the each digester was collected by liquid (acidified water) displacement method in a graduated flask and measured daily.

3. RESULTS AND DISCUSSIONS:

The data obtained for the experiments, as described in the previous section, can be used to study the performance of each digester used for the biogas prouction. Figure 2 shows, the biogas generation capacity of the mixture of the each waste material and its each component under the category of animal dung in 90 days. It can be seen that among the various waste materials, under the above category, slurry of the horse dung can produce more biogas than other dungs. It may be due to the fact that the horse dung most biodegradable among the above waste materials. The degree of biogas generation capacity of the various types of dungs is found to be in ascending order of

Cowdung < Buffalo dung < Mixture of animal dung < Camel dung < Horse dung

Figure 3 shows, the biogas generation capacity of the mixture of kitchen waste and its each component with cowdung in 90 days. It can be seen that among the various types of kitchen wastes, the slurry of the banana peels with cowdung can produce more biogas than other waste materials. This is due to the fact that the banana peels is more biodegradable than other kitchen wastes. The degree of biogas generation capacity of the different kitchen wastes is found to be in ascending order of

Orange peels < Mixture of kitchen wastes < Tea leaves < Potato peels < Banana peels

It can also be seen from the above figure that a small amount of biogas can be produced from the slurry of orange peels with cowdung. It may be due to toxic effect of the orange peels. So, to produce biogas from the mixture of kitchen wastes, orange peels should be removed.

Figure 4 shows the biogas generation capacity of the mixture of waste flowers and its each component with cowdung for a retention period of 90 days. It can be observed that among the different waste flowers, modar flower can produce maximum amount of biogas. It may be due to the reason that modar flower is most biogeradable among the above waste flowers. The degree of biogas generation capacity of the waste flowers is found to be in ascending order of

Sunflower < Balsam < Mixture of waste flowers < Marigold < Oleander.

Figure 5 shows the biogas generation capacity of the mixture of waste leaves and its each component with cowdung for a retention period of 90 days. It is seen that the slurry of potato leaves with cowdung can produce more biogas than other waste leaves. It is due to the fact that the potato leaf is more biodegradable than other waste leaves. The degree of biogas generation capacity of the different waste leaves is found to be in ascending order of

Radish leaf < Cabbage < mixture of waste leaves <

Banana leaf < Potato leaf

Figure 6 shows biogas generation capacity of the each of best waste material under various groups waste materials. The degree of biogas generation capacity of the most biodegradable waste materials under various categories of waste material is found to be in ascending order of

Potato leaf < Banana peels < oleander < Horse dung

4. CONCLUSIONS:

Based on the results obtained in this study, the following conclusions can be drawn:

i) Animal dungs are most suitable waste materials for generation of biogas.

ii) Orange peels can not be used for the biogas production due to its toxic effect.

iii) The above results were obtained at a specific temperature of 37°C. The biogas generation capacity of the each waste materials will be different at other temperatures.

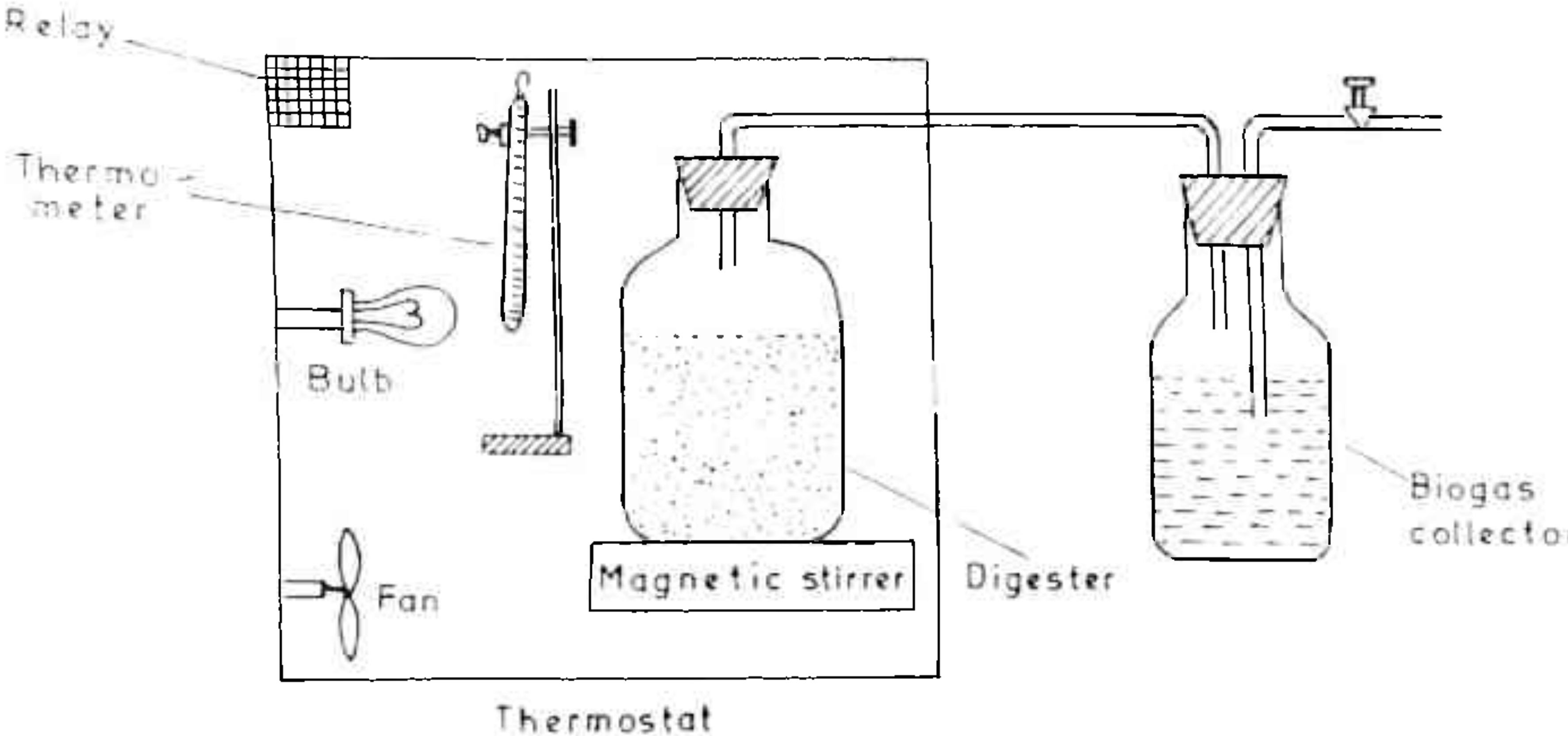
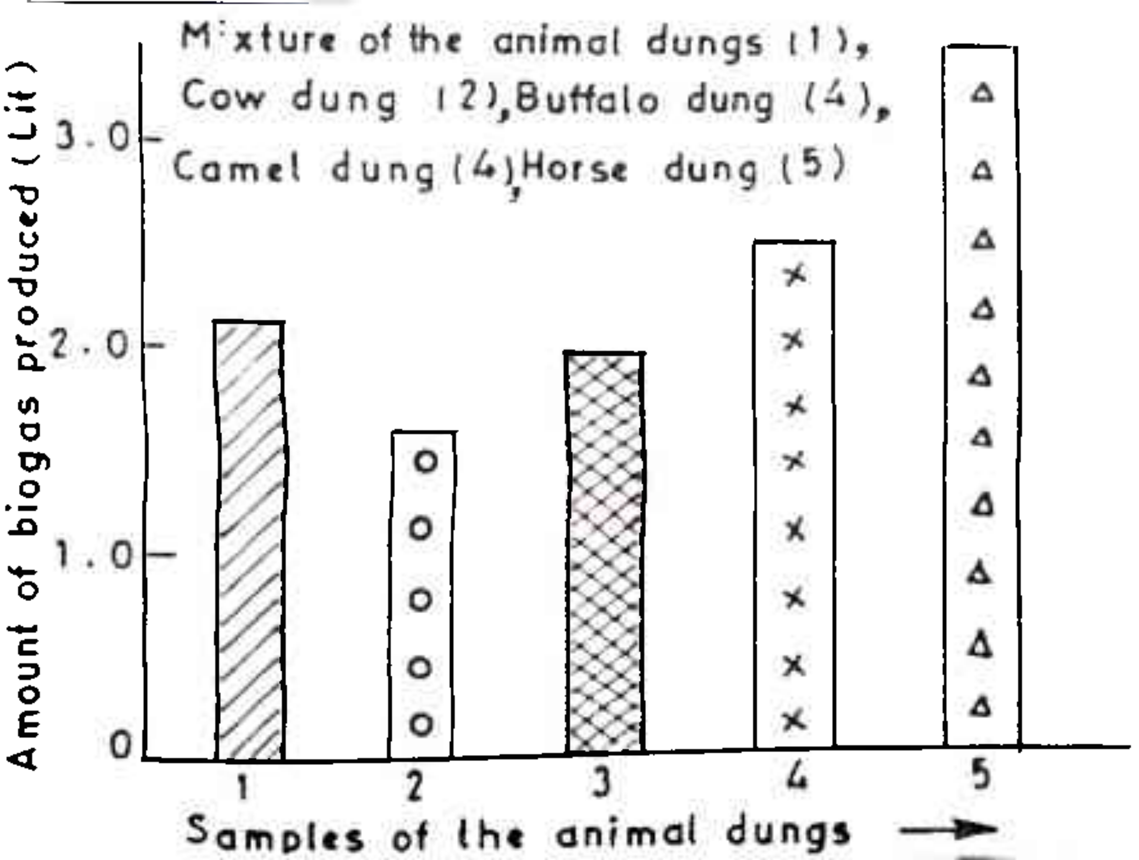


Fig. 1.8 Laboratory scale experimental setup of an anaerobic digester.


M·xture of the animal dungs (1),
Cow dung (2),Buffalo dung (4),
Camel dung (4),Horse dung (5)
Amount of biogas produced (Lit)
3.0
2.0
1.0
0
1
2
3
4
5
Samples of the animal dungs

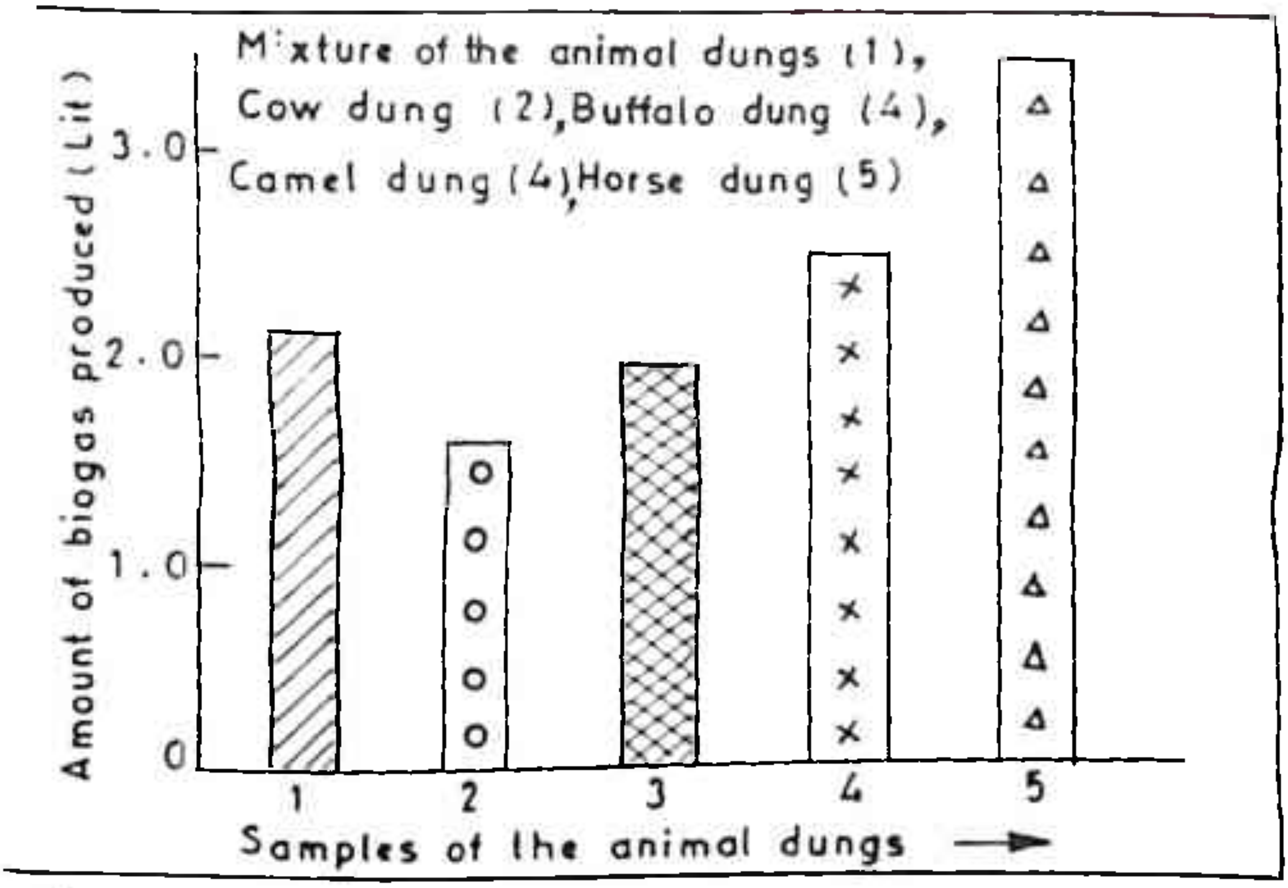


Fig. 2: Biogas generation capacity of the mixture of the animal dungs and its individual components.

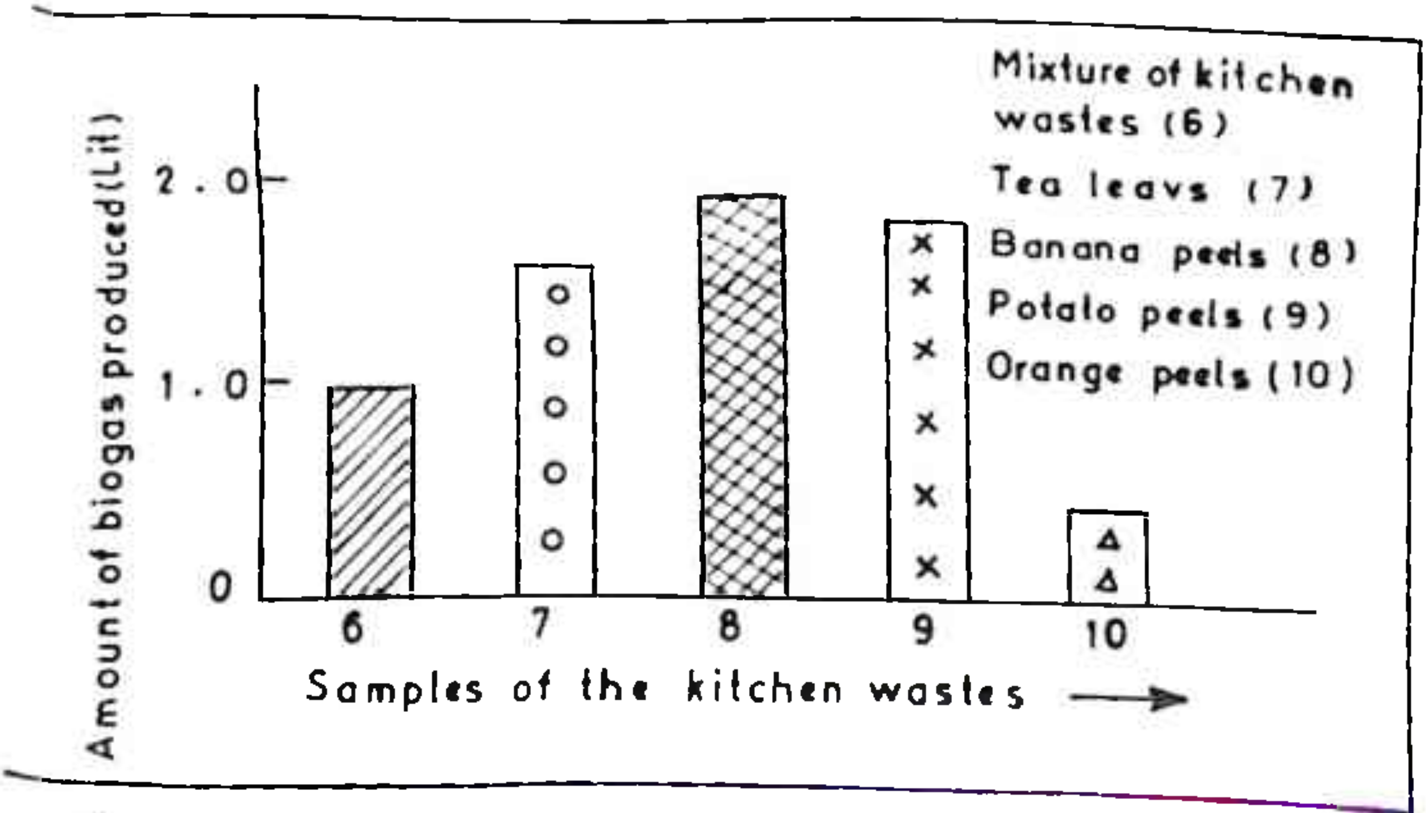
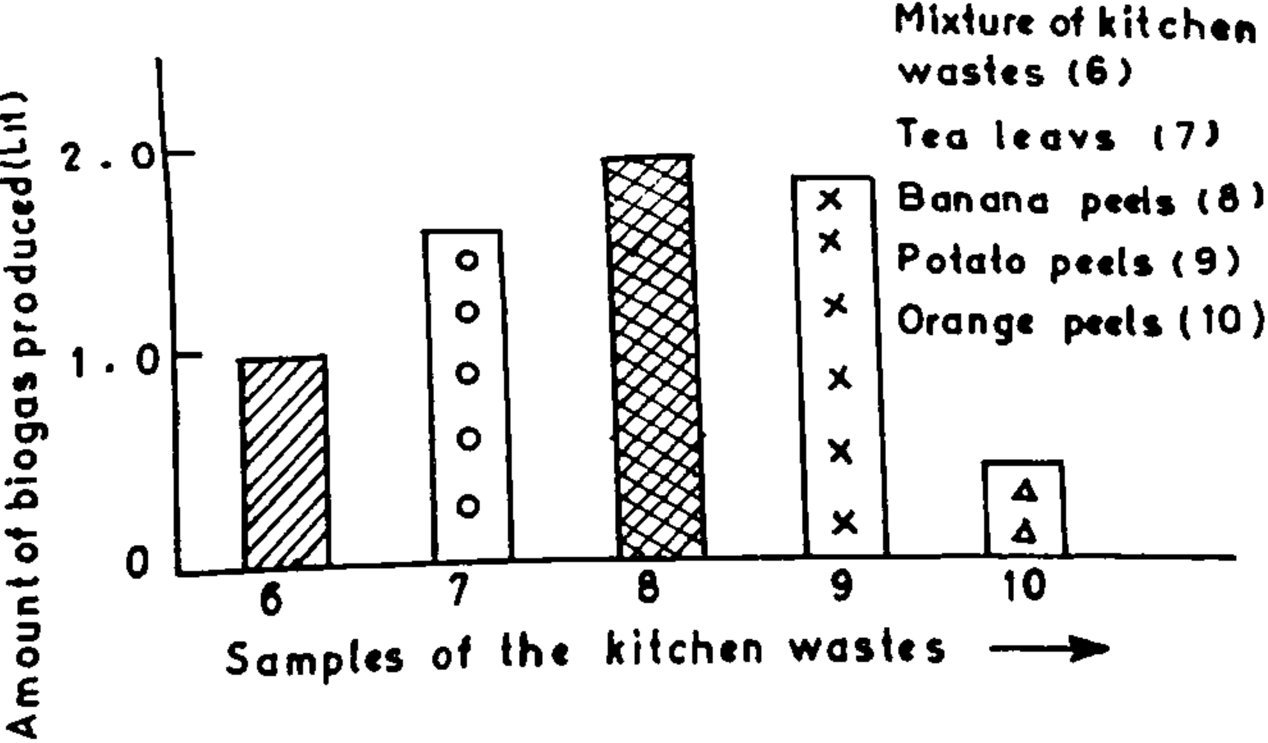


Fig. 3: Biogas generation capacity of the mixture of the Kitchen wastes and its individual components.


Mixture of kitchen wastes (6)
Tea leavs (7)
Banana peels (8)
Potato peels (9)
Orange peels (10)
Amount of biogas produced (Lit)
2.0
1.0
0
6
7
8
9
10
Samples of the kitchen wastes

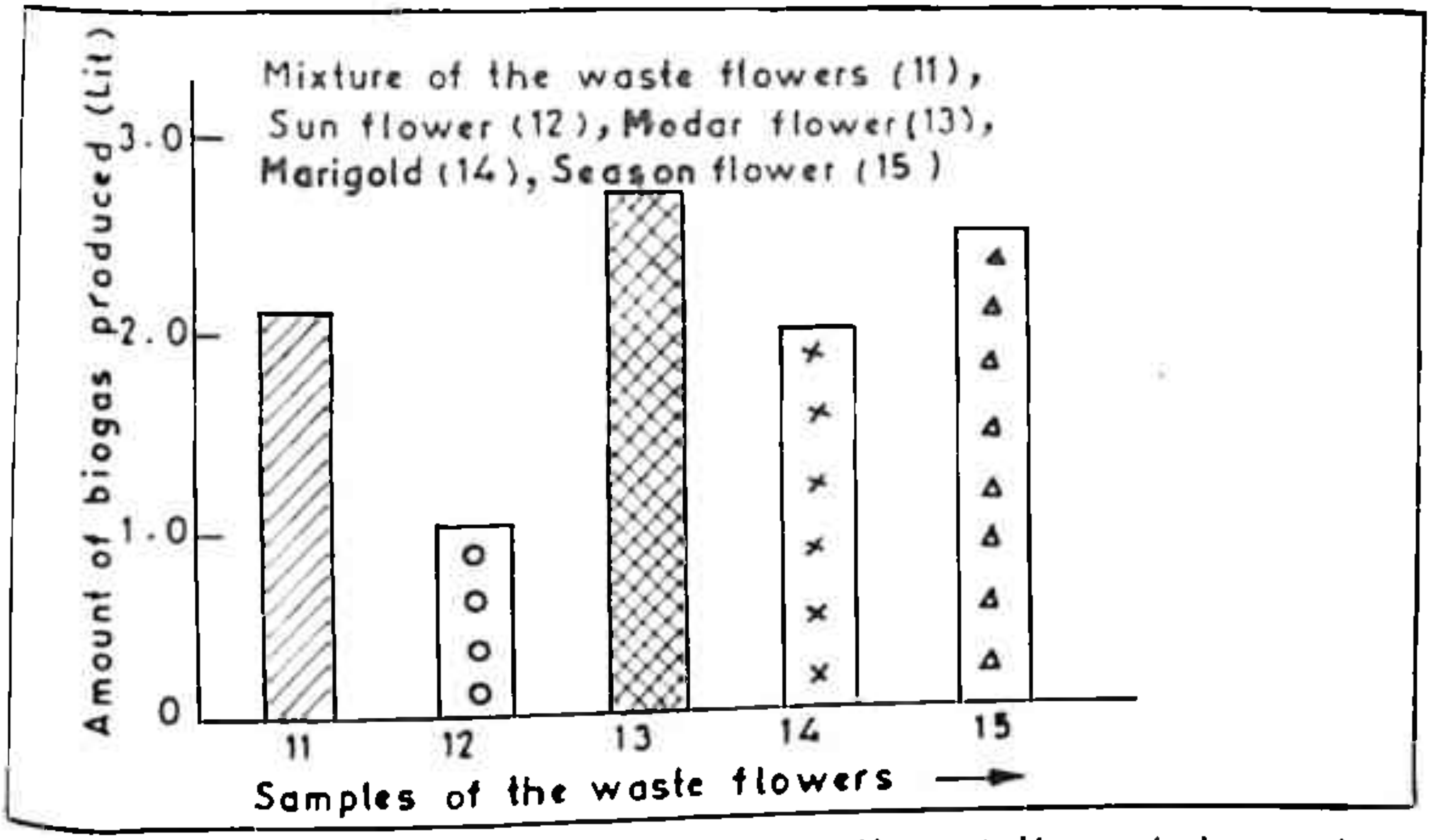


Fig. 4: Biogas generation capacity of the mixture of the waste flowers and its individual components.

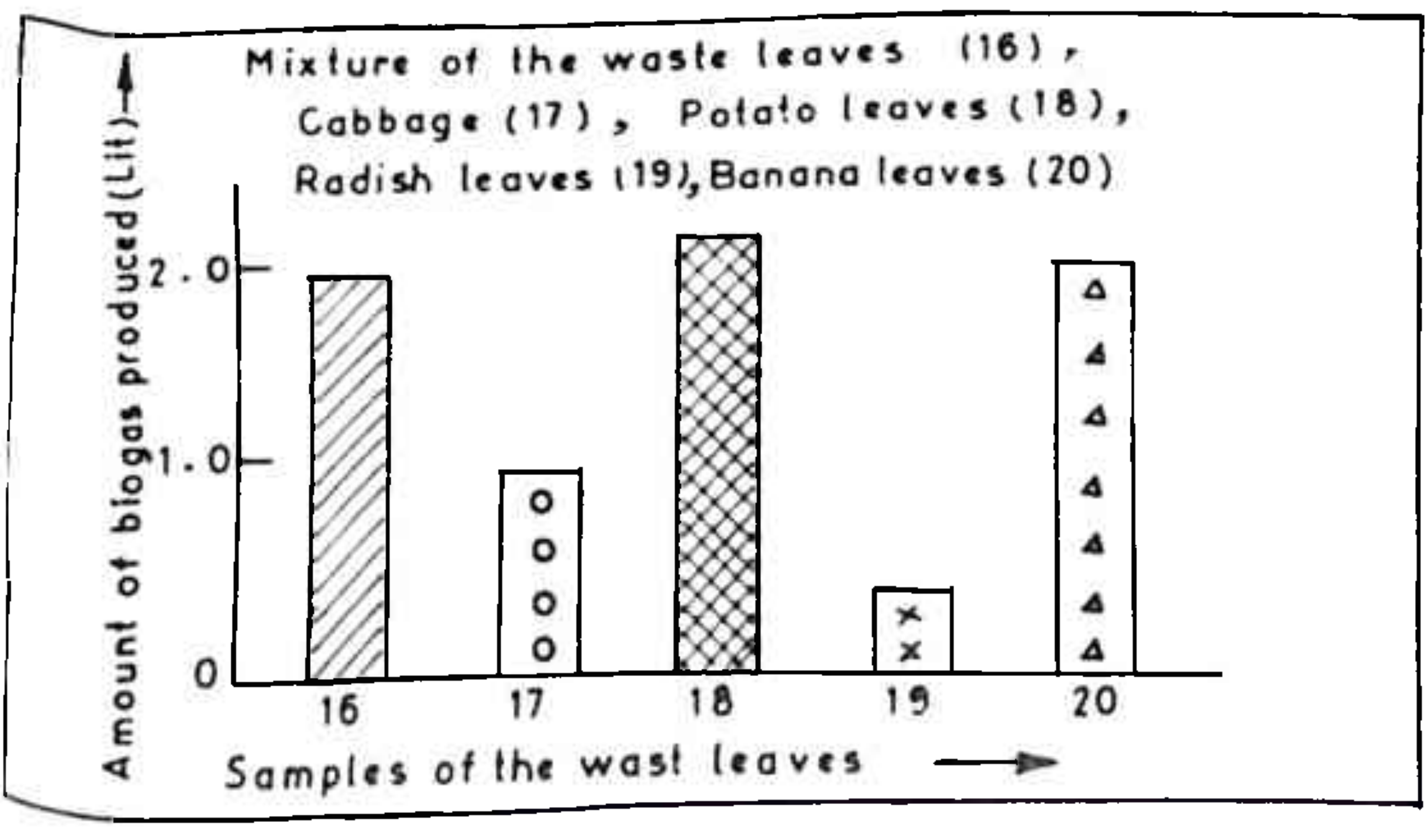


Fig. 5: Biogas generation capacity of the mixture of the waste leaves and its individual compoaents.

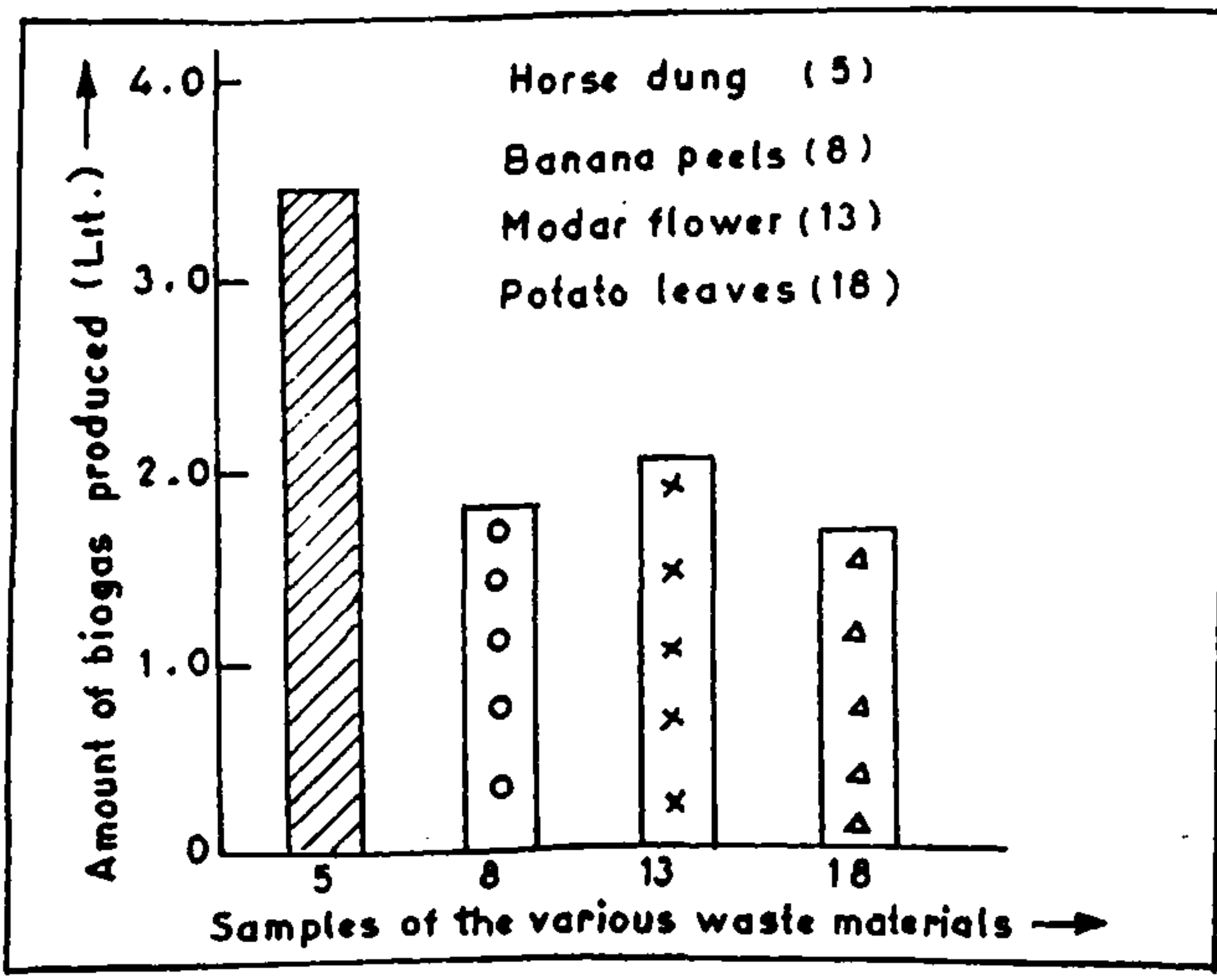


Fig. 6: Biogas generation capacity of the best waste materials under various groups.

REFERENCES:

1. Molnar L. and Bartha I., Solid Waste Methane Generation, Journal of Applied Microbial, Biotechnol 4(4) 481-490 (1988).

2. Shinnawi M.M., et. al., Biogas production from crop residues and poultry wastes, Biomass, Vol. 5, pp 44-48, (1990).

3. Vaviline V.A. et. al., Effective biogas production during anaerobic conversion of complex organic matter, Biomass Vol. 2, pp 48-54 (1994).

4. Owen W.F., Energy in waste water treatment, Prentice Hall of India, pp 21-25 (1982).